

# **Advanced Direct Liquefaction Concepts for PETC Generic Units - Phase II**

**Quarterly Report  
July 1 - September 31, 1997**

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By  
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**ADVANCED DIRECT LIQUEFACTION CONCEPTS  
for PETC GENERIC UNITS  
Phase II**

**Quarterly Technical Progress Report  
for Period July through September 1997**

**by**

**University of Kentucky  
Center for Applied Energy Research**

**CONSOL Inc.**

**Hydrocarbon Technologies, Inc.**

**LDP Associates**

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## ABSTRACT

The results of Laboratory and Bench-Scale experiments and supporting technical and economic assessments conducted under DOE Contract No. DE-AC22-91PC91040 are reported for the period July 1, 1997 to September 30, 1997. This contract is with the University of Kentucky Research Foundation which supports work with the University of Kentucky Center for Applied Energy Research, CONSOL, Inc., LDP Associates, and Hydrocarbon Technologies, Inc. This work involves the introduction into the basic two stage liquefaction process several novel concepts which include dispersed lower-cost catalysts, coal cleaning by oil agglomeration, and distillate hydrotreating and dewaxing. Results are reported from experiments in which various methods were tested to activate dispersed Mo precursors. Several oxothiomolybdates precursors having S/Mo ratios from two to six were prepared. Another having a S/Mo ratio of eleven was also prepared that contained an excess of sulfur. In the catalyst screening test, none of these precursors exhibited an activity enhancement that might suggest that adding sulfur into the structure of the Mo precursors would be beneficial to the process. In another series of experiments, AHM impregnated coal slurried in the reaction mixture was pretreated with  $\text{H}_2\text{S}/\text{H}_2$  under pressure and successively heated for 30 min at 120, 250 and 360 °C. THF conversions in the catalyst screening test were not affected while resid conversions increased such that pretreated coals impregnated with 100 ppm Mo gave conversions equivalent to untreated coals impregnated with 300 ppm fresh Mo. Cobalt, nickel and potassium phosphomolybdates were prepared and tested as bimetallic precursors. The thermal stability of these compounds was evaluated in TG/MS to determine whether the presence of the added metal would stabilize the Keggin structure at reaction temperature. Coals impregnated with these salts showed the Ni and Co salts gave the same THF conversion as PMA while the Ni salt gave higher resid conversion than the other salts and untreated PMA. To activate PMA, a series of sulfided PMA materials was prepared by subjecting the crystalline acid to  $\text{H}_2\text{S}/\text{H}_2$  at 125-450 °C. The chemistries of these partially sulfided materials are reported as well as the reactivity of several impregnated coals. None of the coals impregnated with these sulfided PMA materials gave conversions that exceeded PMA. Reports covering work by the subcontractors for this reporting period have not been received. A report from CONSOL covering a previous reporting period is included.

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## SUMMARY

### TASK 2.1 LABORATORY SUPPORT (UK/CAER)

#### Dispersed Catalyst Studies

Work has continued to define methods to activate Mo precursors to achieve maximum activity within the shortest time. Earlier in this program, it was recognized that Mo catalysts found in the recycle stream were considerably more active in microautoclave runs than obtained with freshly added Mo precursors. More recently we have been examining Mo structures in which all or part of the oxygen had been replaced by sulfur. Several thiomolybdate compounds were made and tested as precursors for liquefaction of BT Wyodak coal. The S/Mo atomic ratio in these compounds varied from two, for ammonium dioxodithiomolybdate ( $\text{MoO}_2\text{S}_2$ ), up to six for  $(\text{NH}_4)_2[\text{Mo}_2^{\text{V}}\text{S}_{12}]\cdot 2\text{H}_2\text{O}$  ( $\text{Mo}_2\text{S}_{12}$ ). One material was prepared with an excess of sulfur (APTM-A), a portion which could be removed by dissolution in  $\text{CS}_2$ . It had a S/Mo ratio of eleven and was also included in the test. Each of these precursors were impregnated onto the coal at concentrations of 300 mg Mo/Kg dry coal. In the absence of added  $\text{H}_2\text{S}$ , both THF and resid conversions increased, though much less than in the presence of  $\text{H}_2\text{S}$ . There was a significant response to increasing S/Mo ratios in these materials, but not sufficient to equal the conversions observed when  $\text{H}_2\text{S}$  is present. In the presence of  $\text{H}_2\text{S}$ , resid conversions for both the 100 and 300 ppm Mo impregnated coals responded to increased S/Mo ratios, although the magnitude was quite small. Thus far, none of these precursors exhibited an activity enhancement that might suggest that adding sulfur into the structure of the Mo precursors would be beneficial to the process.

Another approach to enhance the activity of the Mo catalysts was to pretreat the precursor with  $\text{H}_2\text{S}$  in  $\text{H}_2$  over a range of temperatures. In these runs impregnated coals containing 100 and 300 mg Mo/Kg dry coal were slurried in process oil and exposed to  $\text{H}_2\text{S}/\text{H}_2$  at 2.2 MPA (300 psig). These reaction mixtures were heated successively at 120, 250 and 360 °C for 30 min at each temperature. After pretreatment, the reactor was vented and pressured to 7.0 MPA with  $\text{H}_2$  containing 3 vol%  $\text{H}_2\text{S}$ . The reaction mixture was then subjected to our standard liquefaction run conditions. THF conversions were not affected by this treatment though resid conversions showed a noticeable increase for the 100 ppm Mo impregnated coal. In the past, a higher concentration of fresh Mo was always necessary to achieve the same level of conversion obtained with recycled Mo. This is the first time in the microautoclaves that resid conversions with 100 ppm Mo have reached a level of conversion equivalent to 300 ppm fresh Mo. This suggests that pretreatment is very effective for converting the precursor into an active catalyst.

We are continuing to evaluate phosphomolybdic acid (PMA) as a catalyst precursor since PMA was found to be as effective in promoting the reaction in ALC-2 as ammonium heptamolybdate (AHM). This precursor is especially interesting since its cost differs from AHM by only about 1¢/bbl gasoline product, which reflects the price difference between phosphoric acid and ammonia. Cobalt and nickel phosphomolybdates were prepared and tested as precursors for bimetallic catalysts. In addition, potassium phosphomolybdate was prepared to see the sensitivity of the catalysis reaction to the presence of alkali metals. The thermal stability of these compounds was evaluated in TG/MS

to determine whether the presence of the added metal would stabilize the Keggin structure at reaction temperature. As with PMA, the behavior of Co and Ni salts is similar to PMA in He and H<sub>2</sub>. Apparently in H<sub>2</sub>, the Keggin ion is stable to about 350 °C but loses its constitutional water between 350 and 450 °C. The potassium salt may be quite stable in H<sub>2</sub> up to about 450 °C after which it loses a small amount of weight. Coals were impregnated with these salts to Mo concentrations of 300 mg/Kg dry coal. THF and resid conversions were determined in the Wilsonville Run 262e solvent. The Ni and Co salts gave the same level of THF conversion which was slightly higher than for the K salt. For resid conversion, the Ni salt was the most active with conversion with the Co salt about the same as observed for PMA. We will be investigating the Ni salt further to determine if that activity is legitimate and whether it can be further enhanced.

To activate PMA, we examined H<sub>2</sub>S pretreatment to determine if a more active catalyst could be generated. Several sulfided PMA materials were prepared by subjecting crystalline PMA to flowing streams of H<sub>2</sub>S/H<sub>2</sub> at several temperatures from 125 °C to 450 °C. The amount of exposure to H<sub>2</sub>S ranged from H<sub>2</sub>S/Mo ratios (moles H<sub>2</sub>S/g atom Mo) of 0.3 to 123. S/Mo incorporation ratios ranged from 0.2 to 0.8, which is well below the ratio in MoS<sub>2</sub>. Because of the partial solubility of these sulfided materials, they were impregnated onto coal from aqueous solutions, which involved washing a small amount of the insoluble fraction onto the coal. The activities of the impregnated coals (300 mg Mo/Kg dry coal) were determined using Wilsonville Run 258 solvent in the standard catalyst screening test. The THF and resid conversions for these impregnated precursors were higher for those materials prepared at 125 and 150 °C, which was very nearly the same as observed for untreated PMA. Higher pretreatment resulted in decreased conversions, which may, in part, be related to the decreasing solubility of the precursors treated at the higher temperatures. Unfortunately, none of the conversions exceeded that of PMA itself.

## **TASK 2.1 LABORATORY SUPPORT (CONSOL)**

Determination of phenolics in Run ALC-1 product oils indicates that the phenol deoxygenation activity of the on-line hydrotreater (like the hydrogenation activity) remained high, even though the activity for nitrogen and sulfur removal was low. Characterization showed no evidence that the Mo and Ni in the vacuum bottoms from Run ALC-2 are organically associated. Recent batches of HTI's start-up oil (L-814) are so paraffinic that they would be unsuitable for use by Sandia as a feedstock for hydrotreating tests, as has been proposed.

CONSOL's near-term work plan is to provide assistance to Sandia regarding their hydrotreating tests and to complete the remaining action items from the Run ALC-3 planning meeting. The action items are to: 1) Perform slurry drying tests with agglomerates (tests with two oils at several temperatures each may be conducted). 2) Agglomerate the Ni/Mo-treated coal, and analyze the products to determine if the metals are retained with the coal. 3) Test concepts to reduce the cost of agglomeration (tests may be performed with emulsified oil, recycled water, and aeration).

A paper, "Oil Agglomeration at Low pH as a Pretreatment for Liquefaction of Wyoming (USA) Subbituminous Coal", covering the preparation and use of oil-agglomerated coal in Run ALC-1, was submitted for presentation at the 9th International Conference on Coal Science, September 7-12, 1997, Essen, Germany.

**SECTION ONE**

**UNIVERSITY OF KENTUCKY  
CENTER FOR APPLIED ENERGY RESEARCH**

## Work Performed

### Task 2.1 LABORATORY SUPPORT (UK/CAER)

#### Liquefaction with Mo Precursors Containing Sulfur in the Absence of $H_2S$

We reported previously that resid conversion increased significantly as the S/Mo ratio increased in catalyst precursors while coal conversions were almost unchanged (see Table 1). The catalyst precursors were ammonium heptamolybdate (AHM), ammonium dioxodithiomolybdate (AOTM), ammonium tetrathiomolybdate (ATTM), and ammonium polythiomolybdate (APTM). It was proposed that more active catalyst phases can be formed from precursors already containing sulfur. Also, the sulfur present in the precursor molecules functioned to some extent to protect the active phase from oxygation by water. These experiments were carried out in the presence of  $H_2S$ .

To have a better understand how these precursors function in the absence of  $H_2S$ , a series of runs was made in which  $H_2S$  was not added to the reaction. In these experiments, the active catalyst phase, assuming it incorporates sulfur, would depend only on the sulfur present in the original molecule since no external sulfur source was available.

As usual, in these tests, the coal was impregnated with an aqueous solution of the Mo precursor prior to reaction. The coal paste was dried in a vacuum oven at 20 kPa (125 Torr) and 100 °C for two days to remove water. All of the impregnated coals used in this study were prepared this way and the moisture content was assumed to be zero. In every case, 3 g HTI/BT dry coal, 1.8 g heavy distillate (V1074 heavy distillate from Wilsonville Run 262e), and 3.6 g deashed resid (V1082 deashed resid from Run 262e) were added to the reactor. The reactor was then pressurized with  $H_2$  to 7.0 MPa (1000 psig) at room temperature and the reaction carried out at 440 °C for 30 minutes.

Table 2 shows that, at the catalyst loadings of 300 mg Mo/kg dry coal in the absence of  $H_2S$ , THF conversion increased as the S/Mo ratio increased. Conversions increased significantly for precursors having S/Mo ratios  $\geq 4$ , which is well outside the range of standard deviations shown in Table 2. Another sizable increase was observed for APTM-A. The data on resid conversions do not show a statistical difference between the precursors. Overall, the presence of sulfur is important to both THF and resid conversions whether the sulfur is from  $H_2S$  added to the reactor or from the catalyst precursor molecules. The lower conversions observed in the absence of  $H_2S$  may be due to insufficient sulfur in the reactor to sulfide the precursors and to protect the active phase from being oxidized by the water. Since the fraction of precursor converted to an active phase apparently increased as sulfur increased, THF and resid conversions also increased as the S/Mo ratio in the precursor increased.

Since coal solubilization takes place very early during liquefaction, the small amount of sulfur associated with the precursors maybe sufficient to transform them to an active phase and retain the active phase for a short period. Within that period when conversion is occurring, THF solubilization showed an increase as the S/Mo ratio increased in the precursor. Since resid conversion progresses over a longer period, the active phase may lose sulfur through oxidation by water causing the catalyst to become less active or even inactive. An added source of sulfur is necessary to maintain the catalyst in an active form for resid conversion. Clearly, an external sulfur source is necessary for sulfur

containing precursors already containing a significant concentration of sulfur.

### **Pretreatment of Coal Slurry with $\text{H}_2\text{S}/\text{H}_2$ and $\text{H}_2\text{O}/\text{H}_2\text{S}/\text{H}_2$**

The presence of sulfur is obviously important for the transformation of these oxo and thiomolybdate precursors into an active catalytic phase. The role of water is less clear. However, if we assume, as suggested by Lopez et al.,<sup>1</sup> that the active phase is an oxothiomolybdate, a source of oxygen is necessary to achieve the oxidation. In our system where coal is present, an abundant supply of oxygen is present, either as water or as various carbon-oxygen functional groups. Since Lopez et al. generated active catalysts in petroleum derived oils, which contain little oxygen, water maybe the likely source of the oxygen in their case. It also may be important in our case. Therefore, through judicious exposure of the Mo precursors to  $\text{H}_2\text{S}$  and water, an active precursor may be formed.

A series of experiments was made in which coal slurries containing coals impregnated with AHM and ATTM were pretreated with  $\text{H}_2\text{S}$  and water. Impregnated coals that had been completely dried were slurried in a Run 262 solids-free process solvent and treated in a stream of  $\text{H}_2\text{S}/\text{H}_2$  at a series of temperatures at 2.2 MPa (300 psig). The treat gas was either a water free stream of 8 vol%  $\text{H}_2\text{S}$  in  $\text{H}_2$  or a wet stream of 4 vol%  $\text{H}_2\text{S}/2$  vol%  $\text{H}_2\text{O}/\text{H}_2$ . In a typical run, the reactor was loaded with coal slurry and placed horizontally in a furnace after purging to remove air. The pretreatment was conducted at 2.2 MPa and a gas flow rate of 200 cc/min. The furnace was heated to 120 °C and held for 30 min after which it was successively heated to 250 and 360 °C while holding the temperature at each temperature for 30 minutes. Following 30 min at 360 °C, the reactor was cooled, vented and pressured to 7.0 MPa (1000 psig) with  $\text{H}_2$  containing 3 vol%  $\text{H}_2\text{S}$  (cold). The reactor was then subjected to the base reaction conditions of 30 min at 440 °C.

A blank run was made to determine the effect of pretreating coal for 90 minutes at a sequence of temperatures up to 360 °C. THF and resid conversions for a coal impregnated with AHM to a Mo loading of 100 mg/kg coal were 3.6% and 2.4%, respectively. Therefore, the conversions observed in this series of pretreatment experiments occurred primarily during the 30 min reaction at 440 °C.

Results from this study are shown in Table 3. For all three of the impregnated coals THF conversion was not affected by the pretreatment, as shown in Figure 1. This includes coals impregnated with 100 and 300 ppm Mo as AHM and one impregnated with 300 ppm Mo as ATTM. Resid conversions shown in Figure 2, which are average values of replicated runs, show more spread, although the magnitude of the standard deviations is less than reported in the past, i.e.,  $\pm 4\%$  on maf coal. The most noticeable effect of the  $\text{H}_2\text{S}/\text{H}_2$  pretreatment is a significant increase in resid conversion for the coal loaded with 100 ppm Mo. The resulting resid conversion is the same as that achieved with the coal loaded with 300 ppm Mo. This result suggests that the pretreatment converted a large fraction of the precursor to an active phase. At the 300 ppm Mo loadings for both AHM and ATTM, no apparent advantage was gained from pretreating with  $\text{H}_2\text{S}/\text{H}_2$ .

Result with  $\text{H}_2\text{O}/\text{H}_2\text{S}/\text{H}_2$  as a treat gas shows that the presence of water does not provide an activating effect on the precursor for either the 100 or 300 ppm Mo impregnated coals. For the ATTM impregnated coal, the resid conversion is essentially the same as for the untreated coal. Moisture does appear to negate the effect of the pretreatment. For the 100 ppm Mo impregnated coal, pretreating with  $\text{H}_2\text{O}/\text{H}_2\text{S}/\text{H}_2$  results in a resid conversion that is no different from the untreated

coal but less than the conversion achieved with the  $\text{H}_2\text{S}/\text{H}_2$  treated coal. Apparently in the presence of the moisture the AHM does not activate as well.

The effect of pretreating impregnated coals containing residual moisture with  $\text{H}_2\text{S}/\text{H}_2$  is shown in Figure 3. Coals impregnated with 100 ppm Mo as AHM and containing 9 and 20 wt% moisture are compared with untreated coal and dry coal. THF conversions for these coals are the same but resid conversions differed only for the treated dry coal. Though during the treatment process moisture would likely have been removed at a low temperature, the amount of activation was no different from untreated coal.

It appears that pretreating the coal slurry with  $\text{H}_2\text{S}/\text{H}_2$  improves resid conversion but the presence of moisture is detrimental to forming an active catalyst. Also, high resid conversions can be obtained by using an oversulfided Mo substrate such as APTM-A. Note that these two 100 ppm Mo impregnated coals were as active as the 300 ppm Mo impregnated coals.

	Resid Conv, maf coal
100 ppm Mo as AHM+treatment with $\text{H}_2\text{S}/\text{H}_2$	82.3
100 ppm Mo as APTM-A	82.3
300 ppm Mo as AHM+treatment with $\text{H}_2\text{S}/\text{H}_2$	82.2
300 ppm Mo as AHM	80.3

Apparently, different chemistries are involved in the transformation of AHM and APTM into active catalysts. More research is obviously necessary to understand the structure and mechanism of formation of dispersed catalyst.

### **Liquefaction with Metal Promoted Mo Catalysts**

Phosphomolybdic acid is an interesting Mo-precursor that offers an alternative to the use of ammonium heptamolybdate (AHM) as a Mo source. In both cases, molybdenum trioxide would be the ultimate source of the Mo. Since the trioxide is produced in the original roasting of the molybdenite ore, the cost associated with the precursor would be close to the cost of processing the original ore. Since the trioxide can be readily dissolved in either ammonium hydroxide ( $6 \text{ NH}_3/7 \text{ Mo}$ ) or phosphoric acid ( $\text{H}_3\text{PO}_4/12 \text{ Mo}$ ), the heptamolybdate or phosphomolybdate would never be isolated but used as the aqueous solution. The additional chemical costs associated with dissolving the trioxide with ammonia and phosphoric acid would add only approximately 2 and 3 cents per barrel gasoline cost, respectively, as estimated by LDP Associates. Additional equipment costs would also be quite small and should add little to the overall dispersed catalyst cost.

PMA impregnated coals had previously been reported to give THF and resid conversions that are equivalent to Molyvan L and Molyvan A, both at concentrations of 100 ppm Mo/Kg dry coal. Results from ALC-2 confirmed that the activity of PMA impregnated coal was equivalent to other impregnated precursors and essentially the same as the ALC-1 reference catalyst, which was 1% Fe as  $\text{FeOOH}$  and 100 ppm Molyvan A. In order to expand our work to other PMA type structures, several salts of this family of materials have been investigated to determine if more active catalysts can be generated.

### Preparation and Analysis of PMA Salts

All three salts were prepared by reacting stoichiometric equivalents of the metal carbonates with PMA. For the potassium salt, KPM was precipitated, separated and washed. The Ni and Co salts were both soluble and were isolated by evaporating the solutions to dryness. Elemental analyses and the theoretical molecular formulas for the Co, Ni and K salts as prepared in our laboratory are shown in Table 4. From elemental analysis, the structures of each salt based upon a Keggin configuration with 12 Mo atoms were:

Co salt (CoPM)	$H_{7.5}Co_{2.2}P_{0.92}Mo_{12}O_{40} \cdot 13.5H_2O$
Ni salt (NiPM)	$H_{3.0}Ni_{2.56}P_{0.93}Mo_{12}O_{40} \cdot 18H_2O$
K salt (KPM)	$K_{3.2}P_{1.0}Mo_{12}O_{29.5}$
H form (PMA)	$H_{45.6}P_{2.6}Mo_{12}O_{65.8}$ (starting material)

**TG/MS of CoPM:** TG/MS analyses were performed on each salt both in He and H<sub>2</sub> using a Seiko SSC/5200 thermal analyzer at a heating rate of 20°C/min up to 650°C. CoPM loses 14.3% of its weight when was heated up to 450°C in He. The weight loss occurs via an endothermic process simultaneous with the appearance of water in the effluent gas stream (Figure 4). Most of the loss in weight (92%) occurs up to 350 °C where a small spike appears in the effluent water stream. The total loss of all of the hydrogen plus the portion of oxygen necessary to make H<sub>2</sub>O (32 wt% of the oxygen) corresponds to 14.1 wt% of the starting Co salt, which agrees with the 14.3 wt% loss observed in the TG/MS. Calculating these changes based upon a hypothetical Keggin anion structure, which contains 12 Mo atoms, a total of 17¼ molecules of water are removed. Of this, 16 molecules are removed up to 350 °C with the remaining being removed between 350 and 450 °C. Above 450 °C, the material is stable. Based upon the remaining oxygen in the sample, assuming the remaining solid is a mixture of P<sub>2</sub>O<sub>3</sub>, CoO and a molybdenum oxide (MoO<sub>x</sub>), the oxidation state of the Mo would be +5.4 suggesting that most of the Mo was in a 6+ oxidation state. Due to the presence of the Co ions, it is conceivable that the Keggin structure may still be present at 440 °C, which is the temperature at which the liquefaction reaction is run. Additional data will be needed to determine if the Keggin structure still remains.

The behavior of CoPM in hydrogen up to 450 °C, as shown in Figure 5, is very similar to its behavior in He. The loss in weight of 14.0% is the same as in He. Water appears in the effluent gas as heating begins and continues up to 350 °C with a maximum at 100 °C. A spike in water emission occurs at 180 °C that appears as a shoulder on the m/e 18 water peak in the mass spectrum. By heating to 450 °C, an additional small loss of water occurs. Of the total amount of water lost up to 450 °C, 93% is lost up to 350 °C and the remaining 7% from 350-450 °C. The total weight loss of 14% in the original structure corresponds to a loss of all of the hydrogen plus 32% of the oxygen, which is necessary to make H<sub>2</sub>O. Above 450 °C, further loss in weight is accompanied by the presence of water in the effluent gas stream, which presumably results from removal of oxygen from the structure through reduction of the molybdenum, and possibly phosphorus, by H<sub>2</sub>. This becomes especially important at 550 °C. TG/MS results suggest that the material present at 450 °C is the same as observed in He in which the Mo is largely in a +6 oxidation state. It is conceivable that the Keggin structure continues to exist in H<sub>2</sub> at this high temperature.

**TG/MS of NiPM:** When NiPM was heated in He it loses 14.6% of its weight when heated to 470 °C (Figure 6). Further heating to 600 °C does not result in any further loss in weight. This

14.6% decrease in weight corresponds to a loss of 18.6 molecules of water per the formula shown above. Dehydration appears to occur in two stages. In the first stage, 89% of the water is lost up to 350 °C with the remaining being lost from 350-470 °C. The molybdenum in the solid remaining at 470 °C, assuming it is a mixture of  $P_2O_3$ , NiO and a molybdenum oxide ( $MoO_x$ ), has a +6.0 oxidation state. The formula calculated for this material, ignoring the small excess of hydrogen, is  $Ni_{2.56}P_{0.93}Mo_{12}O_{40}$ , which is surprisingly consistent with the Keggin structure, except for the excess of Ni.

Upon heating NiPM in  $H_2$  up to 360 °C, the sample loses 13.3% of its weight versus 13.0% when heated in He (Figure 7). As before, the mass spectrum of the effluent gas shows the presence of water. The weight loss upon further heating to 470 °C is greater in  $H_2$  (2.7%) than in He (1.6%) which probably suggests that reduction occurred with concomitant removal of additional oxygen. Above 470 °C the loss in weight increases quite dramatically indicating that, unlike CoPM, Ni is promoting both the reduction of Mo and loss of oxygen from the structure. The water peak in the mass spectrum increased quite significantly with a maximum at 600 °C. Based upon the weight loss up to 630 °C and assuming oxygen is lost, the approximate oxidation state of Mo is +2.4. Since weight is continuing to be lost, the Mo is being reduced further.

TG/MS of KPM: The behavior of KPM is considerably different from the Co and Ni salts. Elemental analysis showed this material contained no detectable hydrogen and had an empirical formula of  $K_{3.2}P_{1.0}Mo_{12}O_{29.5}$ . Upon heating in He a loss in weight of less than 3% was observed along with the appearance of water in the effluent gas stream (Figure 8). No other transformations were observed up to 630 °C. In  $H_2$ , an initial loss of weight of approximately 3% was observed after which the material was stable up to 450 °C (Figure 9). Between 450 and 550 °C an additional weight loss of 2.5% occurs. The material present at 450 °C has an oxidation state of approximately +3.4, assuming the solid is composed of  $P_2O_3$ ,  $K_2O$  and  $MoO_x$ , where x is 1.7. At 440 °C, the temperature of the liquefaction reaction, the structure may be largely the Keggin ion.

#### Activity Tests of Co, Ni and K Phosphomolybdates

Metal phosphomolybdate impregnated coals were prepared by the same method used to prepare the starting coals for ALC-2. The coals were impregnated with aqueous solutions of the Ni, Co and K salts. The potassium salt was soluble only after adding a few drops of KOH to the water. Coals were impregnated by adding 0.03 g solution/g dry coal that contained the appropriate concentration of the individual metal salts. The concentration of the salt provided a final loading of 300 mg Mo/kg dry coal. During addition of the solution, the powdered coal was continually stirred to assure even distribution. Impregnated coals were used without being dried and contained 11.9 wt% moisture.

The liquefaction activities of the impregnated coals were determined in 50-cc microautoclaves equipped with a thermocouple and connected to a pressure transducer for monitoring pressure during the reaction. Experiments were run at 440 °C and 9.4 MPa (1350 psig, cold) for 30 min and each was duplicated from 4 to 6 times. In a typical experiment, 1.75 g heavy distillate (V1074 heavy distillate from Wilsonville Run 258B), 2.8 g deashed resid (V1082 deashed resid from Run 258A) and 2.45 g impregnated coal were added to the reactor. The reactor was submerged in a fluidized sand bath and agitated continuously for 30 min at 400 cycles per minute at the specified temperature. At the end of the reaction period, solid and liquid products were removed from the reactor and extracted with THF in a Soxhlet extractor overnight. After removing the solvent from the THF extract, the

liquid product was distilled under vacuum to an atmospheric equivalent endpoint of 524°C.

Nickel phosphomolybdate (NiPM) and cobalt phosphomolybdate (CoPM) gave almost the same average THF conversions, which was somewhat higher than the average conversion for potassium phosphomolybdate (KPM) (see Table 5). The previously reported THF conversion for PMA (92.3%), also shown in the table, was slightly higher than the Co and Ni salts. The standard deviations for the salts showed significant overlap in the values suggesting no significant difference in these conversions, although the PMA value appears to have statistical significance. The difference in average resid conversions of the salts suggested that NiPM was more active than the others, although standard deviations again indicated significant overlap in the values. Compared with previous results on resid conversions with PMA impregnated coal (64.5%), resid conversion for the NiPM is somewhat higher than the others with the Co and K salts being about the same.

### **Liquefaction with Presulfided PMA**

Though polyoxomolybdates have been known to create active dispersed catalysts for both coal and petroleum conversion, the structure and composition of the active catalysts formed from these precursors have received little attention. Because of the unique thermal stability of the polyoxomolybdates, the form of the active catalysts from this family of compounds may be quite different from oxo or thiomolybdates. Likewise, it isn't known whether the corresponding thio analogs of the polyoxomolybdates may be involved in the catalysis reaction. For these reasons, we have investigated the reaction of PMA in the presence of H<sub>2</sub>S-H<sub>2</sub> mixtures. Various sulfided PMA materials have been evaluated for their liquefaction activities. The objective of this study was to understand the form of the catalyst derived from the precursor and hopefully further improve its activity by either altering the reaction conditions or pretreating the precursor.

#### Preparation of Sulfided PMA

Sulfidation experiments were conducted in a 9-inch x 2 inch tubular quartz reactor into which was placed a porcelain boat containing from 1-10 g of PMA. In experiments with one gram PMA, only a thin layer coated the bottom of the porcelain boat. The reactor was placed into a tubular furnace equipped with a thermocouple and temperature controller and a stream of N<sub>2</sub> passed over the sample. After the reactor was purged free of air at ambient temperature, a stream of 8 vol% H<sub>2</sub>S in H<sub>2</sub> was passed over the sample and the reactor heated to the desired temperature. The H<sub>2</sub>S-H<sub>2</sub> mixture was passed over the samples for 1 to 10 hours at 40 to 320 cc/min. In each experiment a total of 19.2 L of H<sub>2</sub>S/H<sub>2</sub> was passed over the sample. Following treatment the reactor was cooled to ambient temperature under flowing N<sub>2</sub> and the products removed. In the experiments the original yellow color changed quickly to green, which lasted for only a short period. All of the samples formed crusty layers that were either dark gray or black in color. The final materials were ground before submitting for analysis. The various methods used to investigate these materials are described below.

#### Analysis of Sulfided Materials

Elemental Analysis: Elemental analyses of the sulfided samples were run either at the CAER or by Galbraith Laboratories. At both laboratories sulfur was determined by combustion in air and molybdenum and phosphorus by inductively coupled plasma emission spectroscopy. Samples analyzed by Galbraith Laboratories had confidence intervals of 5.3, 0.4 and 0.3% for

molybdenum, sulfur and phosphorus, respectively. The Mo and S concentrations in these samples are shown in Table 6. Complete analyses for samples treated at a  $\text{H}_2\text{S}/\text{Mo}$  ratio of 12.3 for 4 hours are shown in Table 7.

**FT-IR Analysis:** FT-IR absorption spectra were obtained with a Fourier transform interferometric spectrometer (Bomem DA3+). For mid-IR measurements, the samples were mixed with 99 wt% of KBr and then pressed into pellets. For far-IR measurements, the samples were mixed with 99 wt% of CsI. A MCT detector and a bolometer were used for mid-IR and far-IR data acquisition, respectively. All spectra were taken at room temperature with an instrument resolution of  $4.0\text{ cm}^{-1}$ .

**Raman Analysis:** Raman scattering measurements were carried out with excitation of an Ar laser (514.5 nm) in the backscattering geometry. The scattered light was analyzed in a Jobin Yvon HR460 single grating spectrometer equipped with a charge-coupled array detector (CCD) and a holographic notch filter (Kaiser Optical). The spectral slit width of the system is about  $2\text{ cm}^{-1}$ . Low laser flux ( $30\text{ mW}/\text{mm}^2$ ) was used to prevent damage to the samples.

**XRD Analysis:** X-ray diffraction data were obtained with a Philips XRG 3100 diffractometer between  $10\text{--}80^\circ$  ( $0.02^\circ$  per step and 2 sec per step). The JSPDS-ICDD Powder Diffraction-2 Database was used for identification of the samples.

#### Characteristics of Sulfided Materials

PMA was treated with  $\text{H}_2\text{S-H}_2$  up to  $450^\circ\text{C}$  for periods from 1-10 hours. Figure 10 and Table 6 show the sulfur uptake of PMA at different sulfidation conditions. The amount of sulfur passed over the samples, expressed as the ratio of moles  $\text{H}_2\text{S}$  per gram atom Mo, ranged from 12.3-122.8.  $\text{H}_2\text{S}$  treatments over this range at different temperatures and for different times does not seem to affect the uptake of sulfur. The S/Mo atomic ratio in the product remains about the same below  $300^\circ\text{C}$  but increases significantly above  $300^\circ\text{C}$ . Increasing the sulfidation time from 1 to 10 hours below  $300^\circ\text{C}$  does not affect the incorporation of sulfur whereas a significant change is observed above  $300^\circ\text{C}$ .

Sulfur incorporation into PMA changes dramatically between 1 and 4 hours but cannot be improved by increasing the treatment time to periods longer than 4 hours. Completely sulfided samples prepared by treating PMA at a  $\text{H}_2\text{S}/\text{Mo}$  ratio of 12.3 for 4 hours were submitted for elemental analysis and subsequently tested for their liquefaction activity. The elemental analyses of these samples are shown in Table 7.

Samples were prepared at temperatures of  $125^\circ\text{C}$  (PMA125),  $150^\circ\text{C}$  (PMA150),  $200^\circ\text{C}$  (PMA200),  $300^\circ\text{C}$  (PMA300) and  $450^\circ\text{C}$  (PMA450). Empirical formulas normalized on the theoretical Keggin ion were calculated from the elemental analyses, i.e., the phosphorus, molybdenum and sulfur contents. The difference between the sum of the concentrations of these three elements and 100% is oxygen and hydrogen. The formula of PMA assumes the excess of phosphorus exists as  $\text{P}_2\text{O}_5$  leaving 23 molecules of crystalline water. In the salts the excess phosphorus in the PMA starting material was not carried over in the salts suggesting that it was solubilized when exposed to water. This is surprising since the Co and Ni salts were prepared by evaporation of the aqueous solutions. The concentration of hydrogen in the sulfided samples was extremely small and was therefore ignored in the calculation. Note that in these samples the excess phosphorus was present at the same concentration as in the starting PMA, i.e., 2.7-3.1 in the sulfided salts vs. 2.6 in the starting PMA. The S/Mo atomic ratio in the products from treating with  $\text{H}_2\text{S}$  at a  $\text{H}_2\text{S}/\text{Mo}$  ratio of 12.3 for 4 hours

ranges from about 0.25 to 0.88 (see Table 6). Also note that the oxygen contents decrease with the sulfidation temperature (see Table 7).

Temperature affects the incorporation of sulfur into the samples. Below 300 °C the S/Mo ratio in the product is about the same but increases sharply at 450 °C. Below 300 °C, the amount of sulfur incorporated is reasonably constant but doubles upon treating at 450 °C. At the higher temperature the sulfur content doubles upon treating from 1 to 4 hours, though in both cases the amount of H<sub>2</sub>S passed over the PMA was the same. Therefore, sulfur incorporation is dependent both on time and temperature.

For samples treated with an excess of H<sub>2</sub>S at a H<sub>2</sub>S/Mo treatment ratio of 12.3, absorptions in the infrared at 1065 and 255 cm<sup>-1</sup> largely disappear upon very mild treatment at 125-150 °C (see Figure 11). These bands have been assigned to the stretching vibrations of the P-O and Mo-O bonds of the P-O-Mo group, respectively, in the Keggin anion.<sup>2</sup> The absorption at 965 cm<sup>-1</sup>, which has been assigned to the Mo-O asymmetric stretching vibration of the terminal oxygen in the Keggin anion, diminishes slightly but remains strong. The Raman spectra of these mildly treated samples show that the Mo-O stretching vibrations at 975 and 995 cm<sup>-1</sup> have markedly decreased. A band observed at 255 cm<sup>-1</sup> assigned to the Mo-O bond of the P-O-Mo group remains strong. A weak shoulder at 225 cm<sup>-1</sup> increased in intensity in both the 125 °C and 150 °C treated materials. Elemental analysis of these samples shows that the compositions have changed through loss of water and addition of 5.0 wt% sulfur (see Table 7). The empirical formula based on the elemental analysis suggests the Mo remains as Mo<sup>6+</sup>.

IR spectra for samples treated at 200 and 300 °C with H<sub>2</sub>S at a 12.3 H<sub>2</sub>S/Mo molar ratio are similar to each other but quite different from the lower-temperature treated materials. The absorption at 865 cm<sup>-1</sup> has largely disappeared and the absorption at 785 cm<sup>-1</sup> has broadened and shifted down field. The intensity of the absorption at 965 cm<sup>-1</sup> has diminished and broadened indicating continued evidence of Mo bonding with a terminal oxygen atom. For the sample treated at 300 °C, absorptions in the Raman spectrum in the 900-1000 cm<sup>-1</sup> region (see Figure 12) have largely disappeared. The doublet at 225 and 255 cm<sup>-1</sup> has also disappeared. Elemental analysis shows that the oxygen concentration decreased relative to the amount in the 125-150 °C treated samples and the average oxidation state of Mo is less than 4+. XRD showed these samples are amorphous.

The IR spectra of the sample treated at 450 °C, with an excess of H<sub>2</sub>S at a H<sub>2</sub>S/Mo ratio of 12.3, shows a weak absorption at 750 cm<sup>-1</sup>. This suggests the presence of Mo-O bonded structures. A weak absorption at 375 cm<sup>-1</sup>, also observed in the sample treated at 300 °C, is consistent with a Mo-S stretching frequency for MoS<sub>2</sub>.<sup>3</sup> The presence of MoS<sub>2</sub> is further confirmed by the appearance of a doublet at 380 and 405 cm<sup>-1</sup> in the Raman spectra (see Figure 12).<sup>4</sup> XRD shows the material produced at 450 °C is amorphous.

#### Activity of Presulfided PMA

The activities of the presulfided materials were determined by adding these particulate solids to the reaction mixture and by impregnating them from an aqueous solution onto coal. Adding the particulate presulfided materials directly to the reaction mixture resulted in a level of activity that was much less than observed by impregnating untreated PMA onto coal (Table 8). Overall, THF

conversions of these sulfided materials decreased as the treatment temperatures increased. Coal conversions were about 60% for materials treated between 125 and 200°C and dropped to about 55% for materials prepared at 300 and 450 °C. The THF conversion for untreated particulate PMA was 80.7%. Resid conversions (maf) for the sulfided materials varied between 40-52% while untreated particulate PMA gave 42.7%.

Coals impregnated with the sulfided materials were prepared by adding 5 mL of a solution containing the sulfided material onto 10 g of dry coal. Any undissolved material, which was normally quite small, was washed onto the coal with additional water. The coal was mixed continuously until it lost excess water and dried in a vacuum oven at 96°C and 33 kPa overnight to remove essentially all of the moisture. The activity of the impregnated sulfided materials was higher activity than observed for the particulate addition runs discussed above. However, the activity still did not reach the level observed for PMA impregnated coal (Table 9). Both THF and resid conversions were higher for those materials prepared at the lower temperatures. THF conversion for PMA125 is only slightly less than the PMA impregnated coal, i.e., 89.2 and 92.3%, respectively. Resid conversions varied from 65 to 42% with PMA125 and PMA150 giving essentially the same resid conversion as PMA impregnated coal (64.5%). Higher treatment temperatures resulted in a significant decrease in resid conversions. Although the data indicate that the sulfided materials when prepared at reasonably low temperatures are as active as PMA, they do not show any improvement over impregnated untreated PMA.

### **Long-residence time studies**

This quarter, coal liquefaction studies were begun on a larger scale, using a 50g charge of moisture-free coal mixed with 50g of deashed resid from Wilsonville Run 258A as solvent. The first coal liquefaction run made with continuous hydrogen feed gas was with the simplest of the catalyst systems evaluated in ALC-2-2: ammonium heptamolybdate added without co-metals. The coal was liquefied in a 300 ml CSTR at severe conditions (440°C for 2 hours). The reactor system had been recently modified to provide for a continuous H<sub>2</sub> gas supply during the experiment, to ensure sufficient hydrogen was present in the reaction mixture to avoid potential retrogressive polymerization of the feedstock. (Experience to date with the microautoclaves used in coal liquefaction studies has not indicated problems in this area, however).

The aims of this run were several-fold:

- to gain operational experience with the newly modified reactor system,
- to provide larger samples produced at severe condition for subsequent analysis of products and in particular, particle size studies of the reactor residual materials, and
- to reproduce the performance of the coal feedstocks in Advanced Concepts run ALC-2, performed at Hydrocarbon Technologies, Inc. (HTI) in November/ December, 1996.

### **Preparation of coal**

Coal feedstock was prepared to have a Mo content of 193 ppmw (mf coal basis), with a final moisture content of 13.2 wt%. The starting coal had a moisture content of 8.9 wt%. This level of Mo replicates previous in-house work with microautoclave liquefaction studies, and is sufficient to cause an observable catalytic effect. The lower 100 ppmw Mo level used in the HTI run has, in previous microautoclave studies, sometimes produced little or no significant catalytic effect. An

impregnating solution was prepared by mixing 0.123 g ammonium heptamolybdate in 10 ml distilled, deionized water. From this solution, 3 ml were added to 114.812 g as-received Black Thunder coal. 100g of the resulting preparation, labelled L-904 [same as HTI's feed coal label] was subsequently added to the reactor without additional drying.

### System Operation

CAER's hydrotreating apparatus is shown in Figure 13. After charging the reactants, the reactor was closed using 45 ft-lb torque on the studs, then the system was purged once to 1.2 MPa (150 psig), and twice to 1.7 MPa (250 psig) with N<sub>2</sub>. The reactor was then purged to 1.7 MPa with hydrogen gas, followed by high pressure testing with H<sub>2</sub> at 10.4 MPa (1500 psig). After system pressure integrity was verified, the mass flow controller was calibrated in the "flow rate display" mode at 1.7 sLpm with a bubble flow meter, flowing hydrogen with a supply pressure of 17.3 MPa (2500 psig). Gas calculations were performed after correcting volumes to standard conditions (standard liters per minute, sLpm) at 0 °C and 101 KPa. A meter calibration factor was calculated as shown in Equation 1 to be 1.0776.

$$MeterFactor = \frac{Actual\ Measured\ Rate,\ sLpm}{MFC\ Display,\ sLpm} \quad Eq.\ (1)$$

Subsequently, the vent meter was calibrated using the mass flow controller in the "flow totalizer" mode by allowing the system to depressure 1.5 MPa (200 psig), then repressuring to the start pressure and temperature with the mass flow controller. The system temperature and pressure, as well as the vent meter temperature and pressure, were carefully noted during this test. A meter factor of 0.984 was calculated for the vent meter using the mass flow controller corrected total, as shown in Equation 2.

$$MeterFactor = \frac{Corrected\ (with\ meter\ factor)\ Repressure\ Volume,\ sL}{Corrected\ (flowing\ T,P)\ Metered\ Volume,\ sL} \quad Eq.\ (2)$$

Following the meter tests, the reactor was depressured to atmospheric pressure. Repressuring began at a rate of 1.7 sLpm H<sub>2</sub> up to a pressure of 7.0 MPa (1000 psig), where the gas flow rate was reduced to 0.2 sLpm. At that time, the reactor temperature program was started, the system heat tapes were energized, and the flow was begun through the DMDS vaporizer. Data was collected at 10 minute intervals. The amount of H<sub>2</sub>S present in the gas feed was controlled by varying the vaporizer temperature between 90 and 110 °C. The reactor heated up to 440 °C in about 2 hours, 40 minutes, and at that time gas was allowed to begin exiting the system; the designated run time was begun. Pressure in the reactor was controlled manually from 16.3 to 17.0 MPa (2350 to 2450 psig) using an exit gas needle valve. The spring loaded back pressure regulator is normally kept at approximately 18.0 MPa (approximately 2600 psig) to give some overpressure protection and prevent the reactor rupture disk (approximately 18.0-20.1 MPa) from venting.

During the run, three gas samples were collected from the back pressure regulator sample point. The first was a 3 L sample collected in a 10 L acrylic gas sample piston over the course of the first 10

minutes of reaction. The second was a 9 L composite, but collected over the remainder of the run time while the reactor was at temperature. The third was collected after the system was cool and in proportion to the amount of gas that was vented to return the system to atmospheric pressure. This last typically comprises 0.5 L samples of the cooled reactor gas collected every 2.2 MPa (300 psig), with the final gas sample collected at 1.7 MPa (10 psig), as the system is depressured (a total of 3 L for this run). Standard 10 L acrylic gas sample cylinders were used as before with the microautoclaves to collect the gases.

At shutdown, all heating power was disconnected, reactor insulation was carefully removed, the vent line was closed, the inlet H<sub>2</sub> line was closed, and the reactor was allowed to air cool to 300°C, at which time ice water was used to further cool to ambient conditions. After a final set of data was collected, the gas supply was switched to N<sub>2</sub>, and ~8L were swept through the system before opening.

#### Product work-up

Reaction products were recovered in three portions: reactor dry scrape, combined reactor and distillate accumulator THF scrape, and distillate accumulator dry scrape. Each product fraction was weighed. Except for the small THF scrape material sample, each product fraction and the feedstock was analyzed by proximate and ultimate analyses, and SIMDIS. For calculation purposes, the THF scrape fraction was assumed to have the same composition as the bulk reactor dry scrape product. Prior to weighing, this material was distilled to 70°C at 15 in Hg vacuum to remove the THF. Also, the distillate accumulator dry scrape was further separated into two fractions that were analyzed separately, the supernatant hydrocarbon fraction and the heavier aqueous layer. Since the fractions weren't weighed when separated, the material balance assumes equal weights of each were recovered.

Gases were analyzed using a Carle gas chromatograph, as before in the microautoclave studies. The amount of DMDS remaining in the vaporizer was measured using a graduated cylinder. This volume was subtracted from the volume charged, and the difference was converted to weight using a density of 1.06 g/ ml.

#### Results and Discussion

Table 10 provides the ultimate analyses of experimental feedstocks and products. The overall material balance as shown in Table 11 was 91%. Carbon was close to this value at 87%, the overall hydrogen balance was 100%, and the ash balance was 118%. These values are reported here without adjustment, or forcing any of the elements to 100% by the addition of product (eg, water make).

Key calculated results for this run are shown in Table 12. Coal conversion was calculated by THF extracting the dry reactor scrape product and ashing the insoluble material. The deashed resid had been earlier found to contain only 0.35% IOM, and that small portion was assumed to remain unconverted for this calculation. A 3.2 g sample was Soxhlet extracted, and 3.0 g were recovered in the thimble after extraction. About 95% was THF insoluble, inferring very little coal conversion. This insoluble portion contained 6.92% ash (as-is), resulting in an estimated coal conversion of only 25.8%.

This is a remarkable result considering the associated high 524 °C+ resid conversion (61.5%) in this run. A check of the reaction product weights shows that nearly all of the 524 °C+ material remaining in the reactor at the end of the run was THF insoluble. This is corroborated by a reasonably good ash balance (needed for the THF conversion calculation); the very high fixed carbon content of this sample, 73.7%; and the SIMDIS curve for the dry reactor scrape sample, shown in Figure 14. There it is seen that nearly 77% of that material did not elute (like a paraffin hydrocarbon boiling above 750 °C), with only 2.4% boiling below that point down to 524 °C.

Against this, a large quantity, 31 g, of light boiling material was collected in the distillate accumulator, suggesting that perhaps the *ca* 50 g remaining in the reactor was at the minimum required for good continuous stirring of the sample. In any event, further study is necessary to explore this unusual result, either with shorter run times or larger reactor charges.

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Table 1. Effects of S/Mo Ratio in Mo Precursor on Liquefaction in Wilsonville Run 262e Solvent in the Absence of H <sub>2</sub> S.						
Catalyst loading, Mo (ppm)	300					
precursor	none	AHM	AOTM	ATTM	APTm-P	APTm-A
S/Mo atomic ratio		0	1.9	4.0	4.5	10.9
Products (% maf coal)						
CO+CO <sub>2</sub>	8.6	9.8	9.5	8.9	5.8	10.2
HC Gases	9.1	5.8	8.8	9.0	6.1	9.5
1050- °F	33.2	44.0	41.0	44.3	49.9	45.9
1050+ °F	49.1	40.4	40.8	37.8	38.3	34.3
THF Coal Conv. (%)	59.7	70.3±3.0	70.7±1.6	76.4±1.5	78.6	83.9±0.5
Resid Conv. (%)	24.2	28.5±2.4	28.3±1.6	29.7±0.5	29.4	31.5±2.7
Resid Conv. (% maf coal)	50.9	59.6±4.9	59.2±3.3	62.3±1.0	61.7	65.7±5.3
<p>a. Liquefaction experiments were carried out at 440 °C and 7.0 MPa (1000 psig) H<sub>2</sub> (cold) for 30 minutes, using 3 g BT/HTI dry coal, 1.8 g V1074 heavy distillate from Run 262e, and 3.6 g V1082 deashed resid from Wilsonville Run 262e. Vacuum distillation were performed at an atmospheric equivalent cutpoint of 565 °C. The 565 °C- cut is obtained by difference and includes 565 °C- oil, water, and losses.</p> <p>b. The catalysts were impregnated on coal using the following water soluble precursors: ammonium heptamolybdate (AHM), ammonium dioxodithiomolybdate (AOTM), ammonium tetrathiomolybdate (ATTM), and ammonium polythiomolybdate (APTm). The catalyst loading is expressed as mg Mo/kg dry coal.</p>						

Table 2. Effects of S/Mo Ratio in Mo Precursor on Liquefaction Results with R262 Solvent										
Catalyst loading, Mo (ppm)	100					300				
precursor	AHM	AOTM	ATTM	APT-M-P	APT-M-A	AHM	AOTM	ATTM	APT-M-P	APT-M-A
S/Mo atomic ratio	0	1.9	4.0	4.5	10.9	0	1.9	4.0	4.5	10.9
Products (% maf coal)										
CO+CO <sub>2</sub>	8.3	8.5	8.3	9.2	5.7	7.4	13.1	8.2	8.6	10.2
HC Gases	11.3	9.3	8.8	9.5	9.2	9.9	11.1	7.2	7.6	9.4
1050- °F	54.0	56.7	60.4	57.5	67.4	62.9	58.4	67.6	66.4	68.3
1050+ °F	26.4	25.5	22.4	23.7	17.7	19.7	17.4	17.0	17.4	12.0
THF Coal Conv. (%)	85.6±1.7	86.3±1.1	86.6±0.2	88.6±0.2	87.2±2.6	90.6±0.1	91.2	91.3±1.1	92.2±0.2	91.7±0.3
Resid Conv. (%)	35.2±0.3	35.8±0.5	36.9±0.5	36.5±1.4	39.6±1.5	38.4±0.2	39.5	39.7±1.4	39.5±0.9	42.0±1.3
Resid Conv. (% maf coal)	73.6±0.6	74.5±1.1	77.6±1.1	76.3±3.0	82.3±2.9	80.3±0.4	82.6	83.1±3.1	82.6±1.8	88.0±2.8
<p>a. Liquefaction experiments were carried out at 440 °C and 7.0 MPa (1000 psig) H<sub>2</sub> containing 3 vol% H<sub>2</sub>S (cold) for 30 minutes, using 3 g BT/HTI dry coal, 1.8 g V1074 heavy distillate from Run 262e, and 3.6 g V1082 deashed resid from Wilsonville Run 262e. Vacuum distillation were performed to an atmospheric equivalent endpoint of 565 °C. The 565 °C-cut is obtained by difference and includes 565 °C- oil, water, and losses.</p> <p>b. The catalysts were impregnated on coal using aqueous solutions of ammonium heptamolybdate (AHM), ammonium dioxodithiomolybdate (AOTM), ammonium tetrathiomolybdate (ATTM), and two ammonium polythiomolybdates (APT-M-A and APT-M-P) as precursors. Catalyst loading is expressed as mg Mo/kg dry coal.</p>										

Table 3. Effects of Coal Slurry Pretreatment on Liquefaction with Mo Catalysts in Run 262e Solvent (120, 250, 360°C, each 30 min. )											
Mo catalyst loading, ppm	100					300			300		
precursor	AHM					AHM			ATTM		
Moisture on Dry Coal (%)	0	0	9	20	0	0			0		
Pretreatment	none	H <sub>2</sub> S/H <sub>2</sub>			H <sub>2</sub> O/H <sub>2</sub> S /H <sub>2</sub>	none	H <sub>2</sub> S/H <sub>2</sub>	H <sub>2</sub> O/H <sub>2</sub> S /H <sub>2</sub>	none	H <sub>2</sub> S/H <sub>2</sub>	H <sub>2</sub> O/H <sub>2</sub> S /H <sub>2</sub>
Products (% maf coal)											
CO+CO <sub>2</sub>	8.3	4.2	4.5	3.6	4.4	7.4	2.8	3.5	8.2	3.6	4.4
HC Gases	11.3	8.0	8.8	7.2	5.9	9.9	6.3	6.3	7.2	10.4	8.6
1050- °F	54.0	70.1	57.5	59.4	60.3	62.9	73.1	65.2	67.6	65.4	70.9
1050+ °F	26.4	17.7	29.2	29.8	29.4	19.7	17.8	25.0	17.0	21.1	16.0
THF Coal Conv. (%)	85.6±1.7	87.0±0.5	85.9±1.9	85.4±1.3	84.3	90.6±0.1	89.0±0.6	88.7	91.3±1.0	92.6±2.5	92.9
Resid Conv. (%)	35.2±0.3	39.5±0.8	33.7±0.1	33.5±0.3	33.8	38.4±0.2	39.3±0.8	35.7	39.7±1.4	37.6±1.3	40.2
Resid Conv. (% maf coal)	73.6±0.6	82.3±1.7	70.8±0.1	70.2±0.6	70.6	80.3±0.4	82.2±1.6	75.0	83.1±3.1	78.9±2.5	84.0
<p>a. Liquefaction experiments were carried out at 440 °C and 7.0 MPa (1000 psig) H<sub>2</sub> containing 3 vol% H<sub>2</sub>S (cold) for 30 minutes, using 3 g BT/HTI dry coal, 1.8 g V1074 heavy distillate from Run 262e, and 3.6 g V1082 deashed resid from Wilsonville Run 262e. Vacuum distillation were performed to an atmospheric equivalent endpoint of 565 °C. The 565 °C-cut is obtained by difference and includes 565 °C- oil, water, and losses.</p> <p>b. The catalysts were impregnated on coal using aqueous solutions of ammonium heptamolybdate (AHM), (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O, and ammonium tetrathiomolybdate (ATTM), (NH<sub>4</sub>)<sub>2</sub> MoS<sub>4</sub>, as precursors. Catalyst loading is expressed as mg Mo/kg dry coal.</p> <p>c. Prior to reaction, the coal slurry was pretreated in a tubular furnace at 2.1 MPa (300 psig) and sequentially at 120, 250, and 360 °C for 30 min. at each temperature. The pretreating gas contained either 4 or 8 vol% H<sub>2</sub>S in H<sub>2</sub> and 2 vol% H<sub>2</sub>O. The flowrate of the pretreating gas was 200 sccm.</p>											

Table 4. Elemental analysis of metal salts of PMA

Material	Composition, wt%							Formula
	H	P	Mo	Co	Ni	K	O (diff)	Normalized on Mo <sub>12</sub>
PMA *	1.98	3.52	49.65				44.85	H <sub>3.5</sub> PMo <sub>12</sub> O <sub>40</sub> ·P <sub>1.6</sub> O <sub>4</sub> ·21H <sub>2</sub> O
Co salt	1.58	1.29	52.30	5.91			38.92	H <sub>7.5</sub> Co <sub>2.2</sub> P <sub>0.92</sub> Mo <sub>12</sub> O <sub>40</sub> ·13.5H <sub>2</sub> O
Ni salt	1.71	1.25	50.06		6.54		40.44	H <sub>3.0</sub> Ni <sub>2.56</sub> P <sub>0.93</sub> Mo <sub>12</sub> O <sub>40</sub> ·18H <sub>2</sub> O
K salt	<0.5	1.74	64.74			7.02	26.50	K <sub>3.2</sub> P <sub>1.0</sub> Mo <sub>12</sub> O <sub>29.5</sub>
* Theoretical molecular formula for PMA based on Keggin structure: H <sub>3</sub> PMo <sub>12</sub> O <sub>40</sub> · 20H <sub>2</sub> O								

Table 5. Liquefaction activity of PMA salts at 440°C and 9.4 MPa (1350 psig).

	CoPM	NiPM	KPM	PMA
% Coal Conversion	88.5±1.3	88.3±1.8	84.7±2.4	92.3±2.4
% Resid Conversion	31.0±3.4	33.3±2.7	29.9±3.7	
% Resid Conversion (maf)	65.5±7.1	70.6±5.6	63.2±7.7	64.5±5.4
n =	6	5	4	11

Table 6. Sulfur content and S/Mo atomic ratio of sulfided PMA materials.										
Temp., °C	Initial H <sub>2</sub> S/Mo ratio in feed: 12.3 (for 1 g)									
	S wt % in product					S/Mo atomic ratio in product				
	1 h	4 h	6 h	8 h	10 h	1 h	4 h	6 h	8 h	10 h
125	3.78	4.95	-	-	-	0.19	0.25	-	-	-
150	4.27	5.4	-	-	-	0.21	0.27	-	-	-
200	4.46	4.79	3.2	-	-	0.22	0.22	0.16	-	-
300	4.16	4.93	4.35	4	-	0.20	0.22	0.21	0.21	-
450	10.9	20.6	17.25	16	-	0.47	0.88	0.74	0.67	-
	Ratio of moles H <sub>2</sub> S/g atoms Mo in feed: 122.8 (for 1 g)									
125	-	4.37	-	-	-	-	0.22	-	-	-
150	-	3.9	-	-	-	-	0.19	-	-	-
200	-	3.77	-	-	-	-	0.18	-	-	-
300	-	3.69	1.79	4	-	-	0.18	0.09	0.2	-
450	-	14.95	17.1	17.7	18.1	-	0.64	0.73	0.76	0.78

Table 7. Elemental analysis of PMA and the sulfided samples. Ratio of moles H <sub>2</sub> S/g atoms Mo in feed = 12.3 Treatment time = 4 h					
Material	Composition, wt%				Formula
	P	Mo	S	O (diff)*	PMo <sub>12</sub> S <sub>y</sub> O <sub>z</sub>
PMA	3.52	49.65	0.00	46.83	H <sub>45.6</sub> P <sub>2.6</sub> Mo <sub>12</sub> O <sub>65.8</sub> (H <sub>3</sub> PMo <sub>12</sub> O <sub>40</sub> ·20H <sub>2</sub> O)
PMA125	4.26	59.50	4.95	31.29	P <sub>2.7</sub> Mo <sub>12</sub> S <sub>3.0</sub> O <sub>37.8</sub>
PMA150	4.57	60.97	5.40	29.06	P <sub>2.8</sub> Mo <sub>12</sub> S <sub>3.2</sub> O <sub>34.3</sub>
PMA200	4.74	65.60	4.79	24.87	P <sub>2.7</sub> Mo <sub>12</sub> S <sub>2.6</sub> O <sub>27.3</sub>
PMA300	5.48	66.49	4.93	23.10	P <sub>3.1</sub> Mo <sub>12</sub> S <sub>2.7</sub> O <sub>25.0</sub>
PMA450	5.31	70.11	20.60	3.98	P <sub>2.8</sub> Mo <sub>12</sub> S <sub>10.6</sub> O <sub>4.1</sub>
* Difference accounts for oxygen and hydrogen					

Table 8. Activity of sulfided PMA added as particulate catalysts						
	PMA	PMA125	PMA150	PMA200	PMA300	PMA450
% Coal Conv	80.7	60.6	63.9	61.4	54.1	56
% Resid Conv (maf)	42.7	40.7	39.3	51.9	45.3	38.5

Table 9. Activities of coals impregnated with aqueous solutions of sulfided PMA.						
	PMA	PMA125	PMA150	PMA200	PMA300	PMA450
% Coal Conv	92.8	89.2	86.6	73.5	70.4	62.4
% Resid Conv (maf)	64.5	65.4	65.1	51.8	48.4	42.0

Table 10. Ultimate analyses of feedstocks and products (each as-determined).								
Material	Date analyzed	C, wt%	H, wt%	N, wt%	S, wt%	O, wt% (diff)	ash, wt%	Total, wt%
L-904	7/21/97	58.9	5.4	1.1	0.4	29.7	4.5	100.0
R-258A DAR	7/21/97	91.3	6.5	1.2	0.1	0.8	0.1	100.0
DMDS	6/9/95	27.1	6.3	1.8	58.1	6.8	0.0	100.0
reactor dry scrape	7/21/97	89.3	3.8	1.3	0.3	(0.7)	6.0	100.0
distillate accumulator dry scrape tops	7/21/97	79.5	8.9	1.7	2.0	7.9	0.0	100.0
distillate accumulator dry scrape bottoms	7/21/97	1.8	10.9	1.8	0.7	83.7	1.1	100.0

Table 11. Total and elemental material balances, unadjusted.							
Element	C, wt%	H, wt%	N, wt%	S, wt%	O, wt% (diff)	ash, wt%	Total, wt%
Out/in, %	87	100	82	55	94	118	91

Table 12. Hydrotreating results, 300 ml CSTR run.							
Run No.	Feedstock	524°C+ in feedstock, wt% maf feed	524°C+ resid conv., wt% maf feed	THF conversion, wt% maf coal	C <sub>1</sub> -C <sub>3</sub> gas yield, wt% maf feed	H <sub>2</sub> uptake by diff., mg/g maf coal <sup>a</sup>	H <sub>2</sub> balance, (uptake basis), % <sup>b</sup>
K7-192-1	L-904 in R258A DAR	88.8	61.5	25.8	25.3	37	99%
a. Includes the hydrogen associated with the decomposition of DMDS. b. Excludes hydrogen gas calculated to be merely passing through the reactor.							

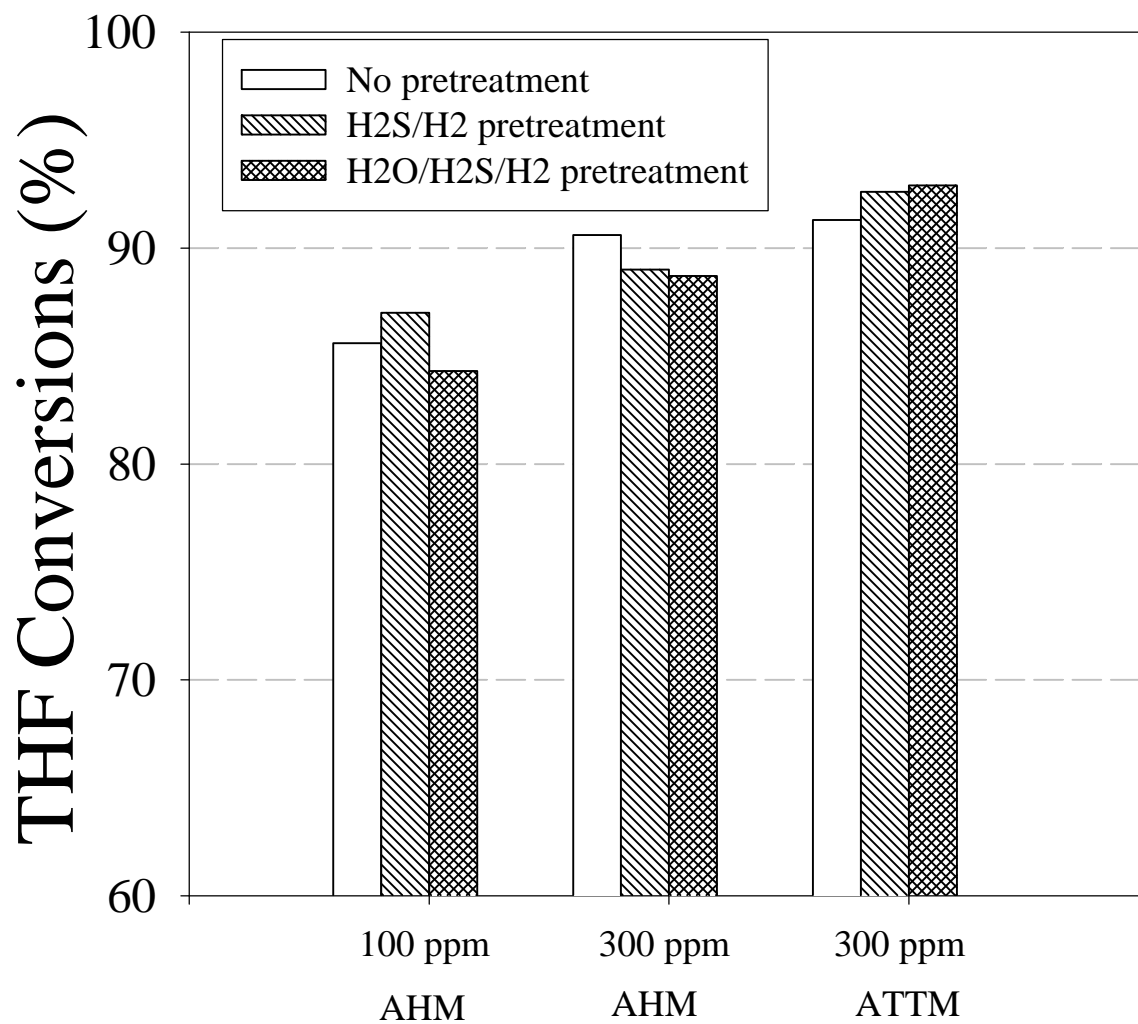


Figure 1. Effect of H<sub>2</sub>S/H<sub>2</sub> and H<sub>2</sub>O/H<sub>2</sub>S/H<sub>2</sub> Pretreatment on THF Conversion in Run 262 Solvent

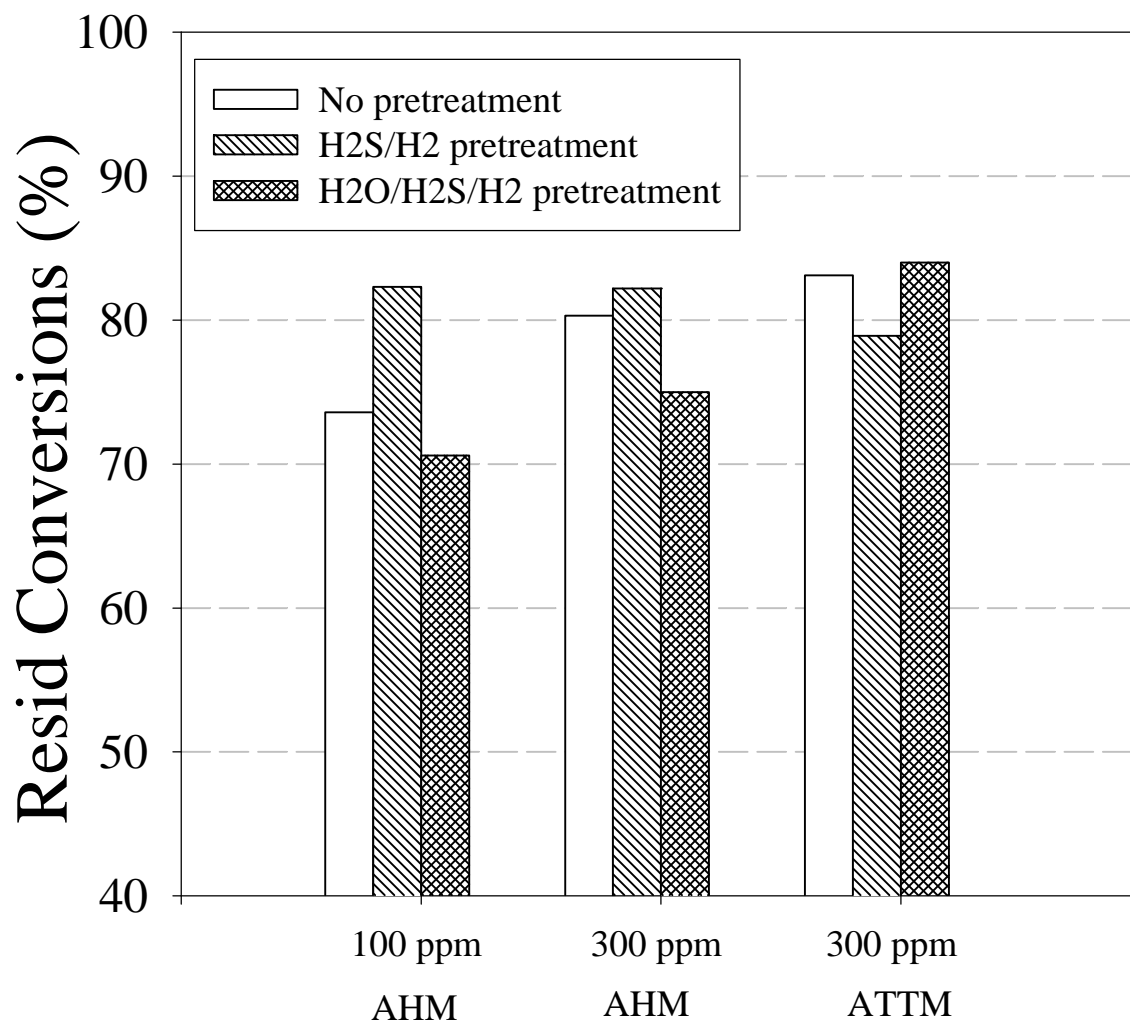


Figure 2. Effect of H<sub>2</sub>S/H<sub>2</sub> and H<sub>2</sub>O/H<sub>2</sub>S/H<sub>2</sub> Pretreatment on Resid Conversion in Run 262 Solvent

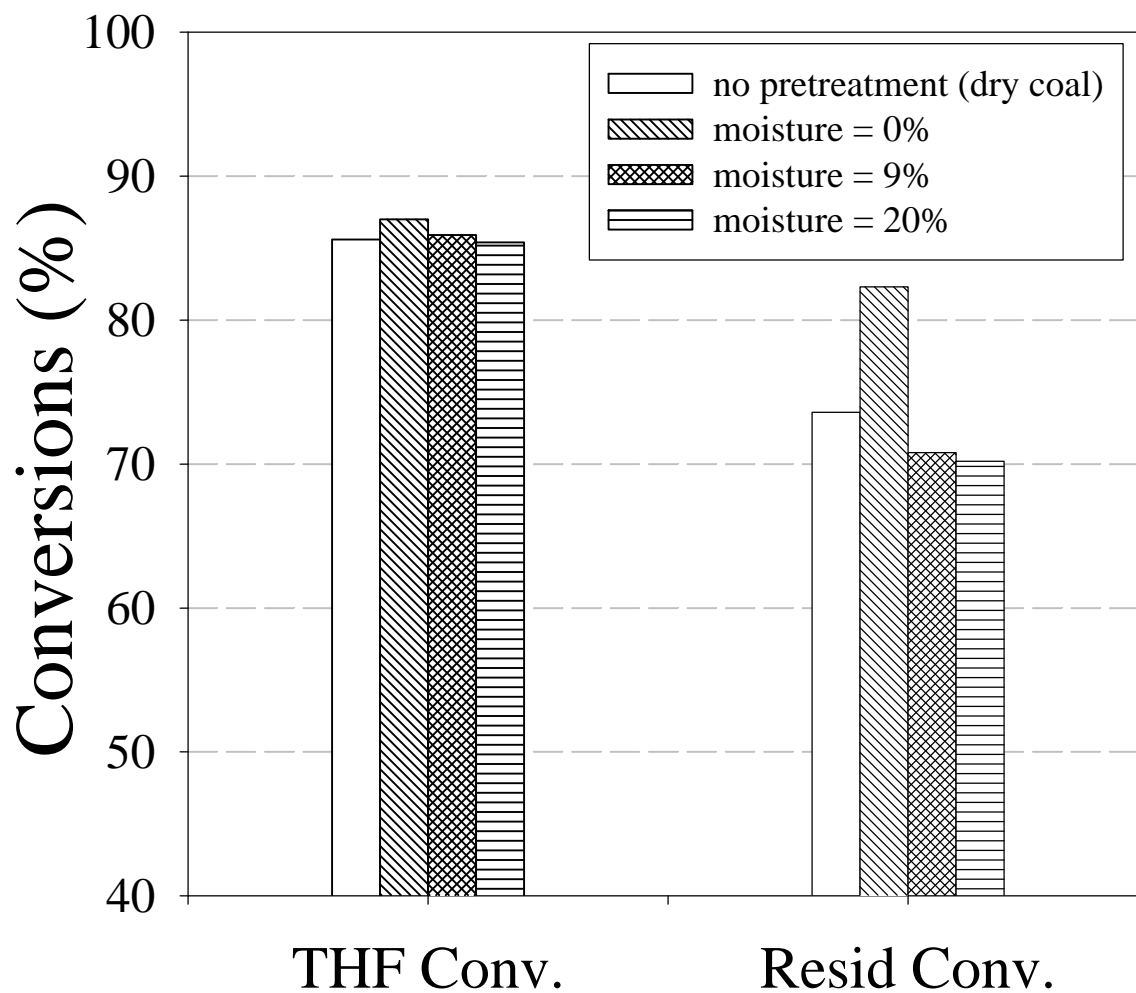


Figure 3. Effect of  $H_2S/H_2$  Pretreatment of Coals with Varying Moisture Contents on Liquefaction in Run 262 Solvent (catalyst loading was 100 ppm Mo on dry coal )

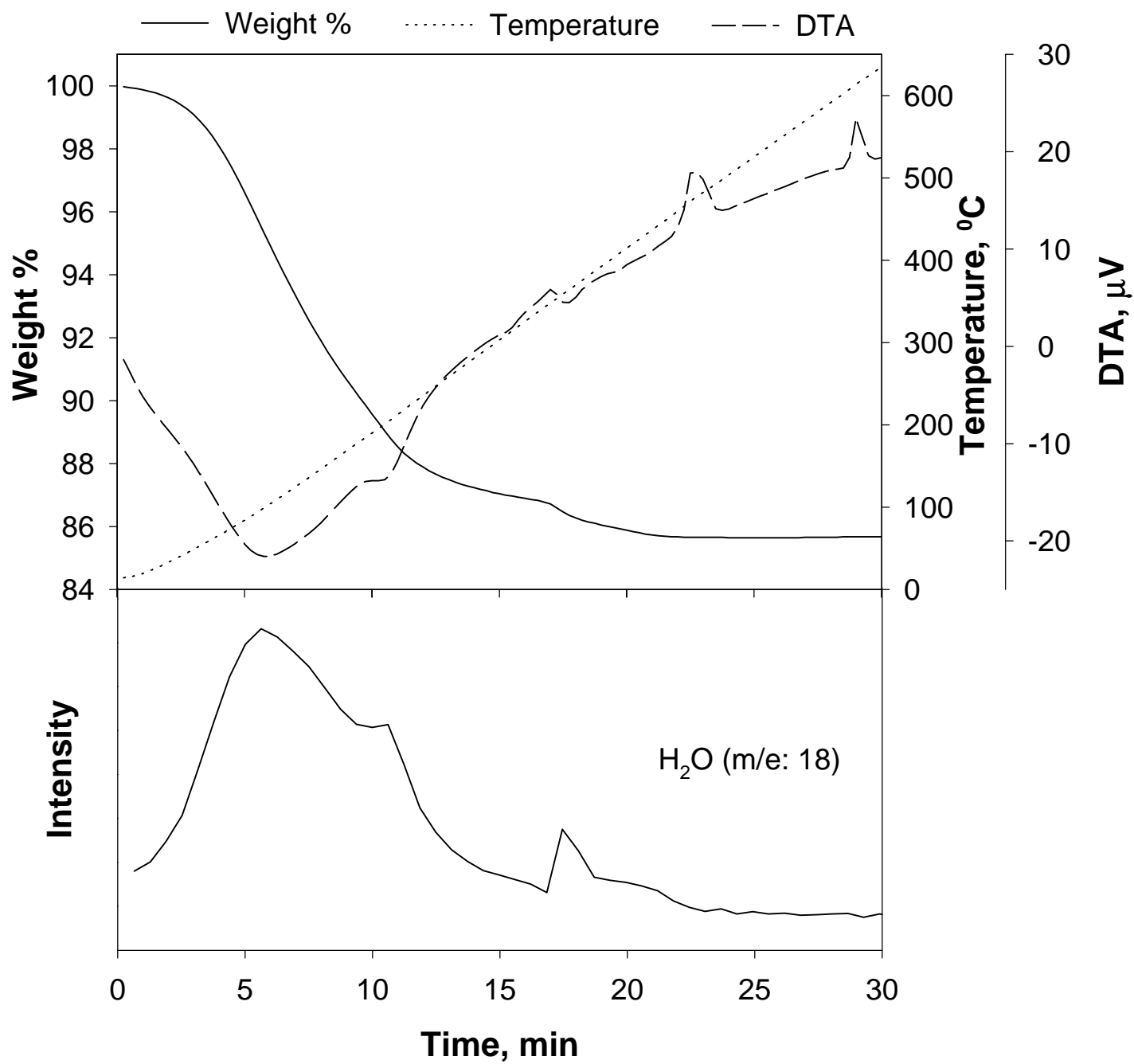


Figure 4. TG/MS spectra of CoPM in He.

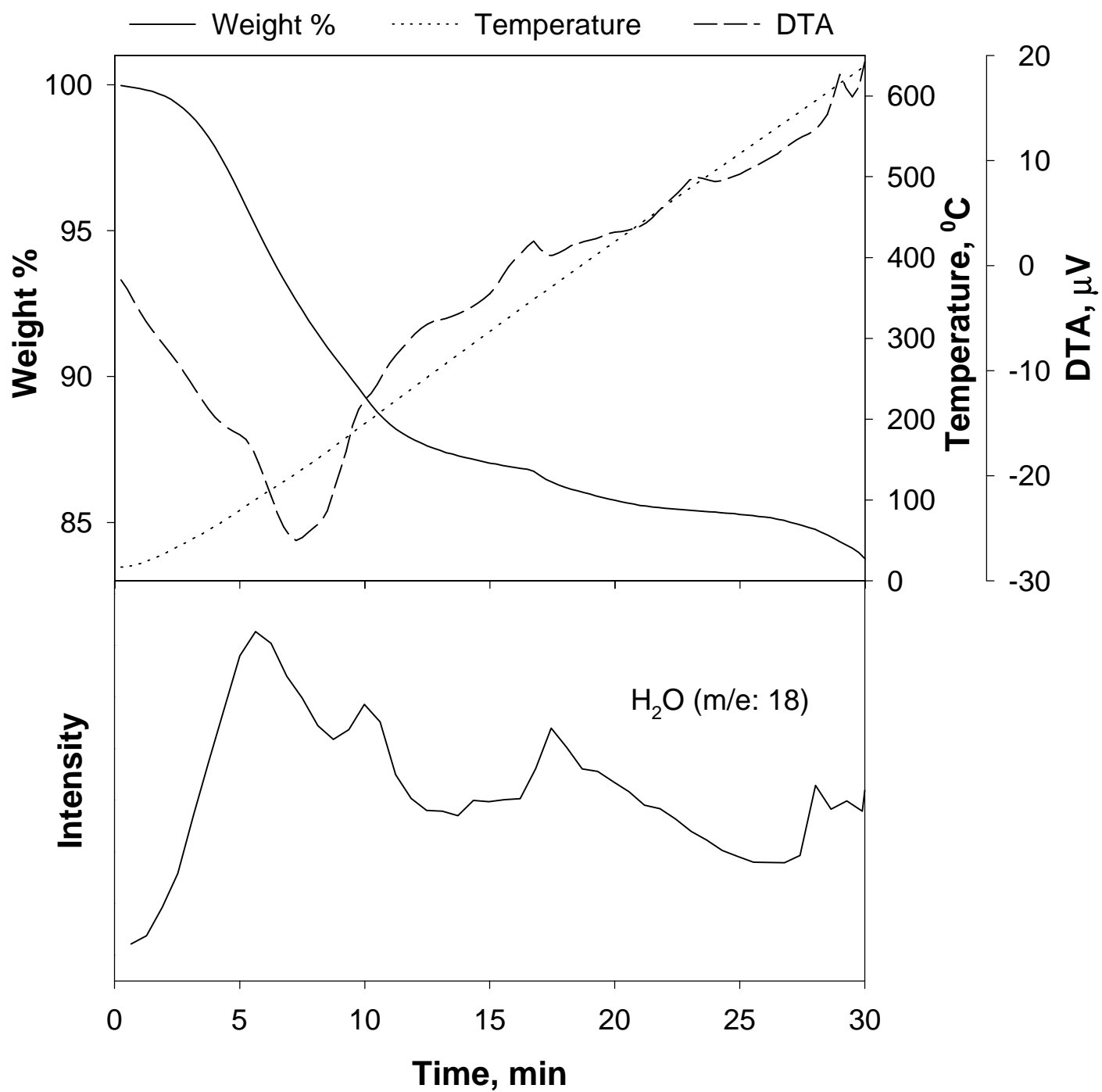


Figure 5. TG/MS spectra of CoPM in H<sub>2</sub>.

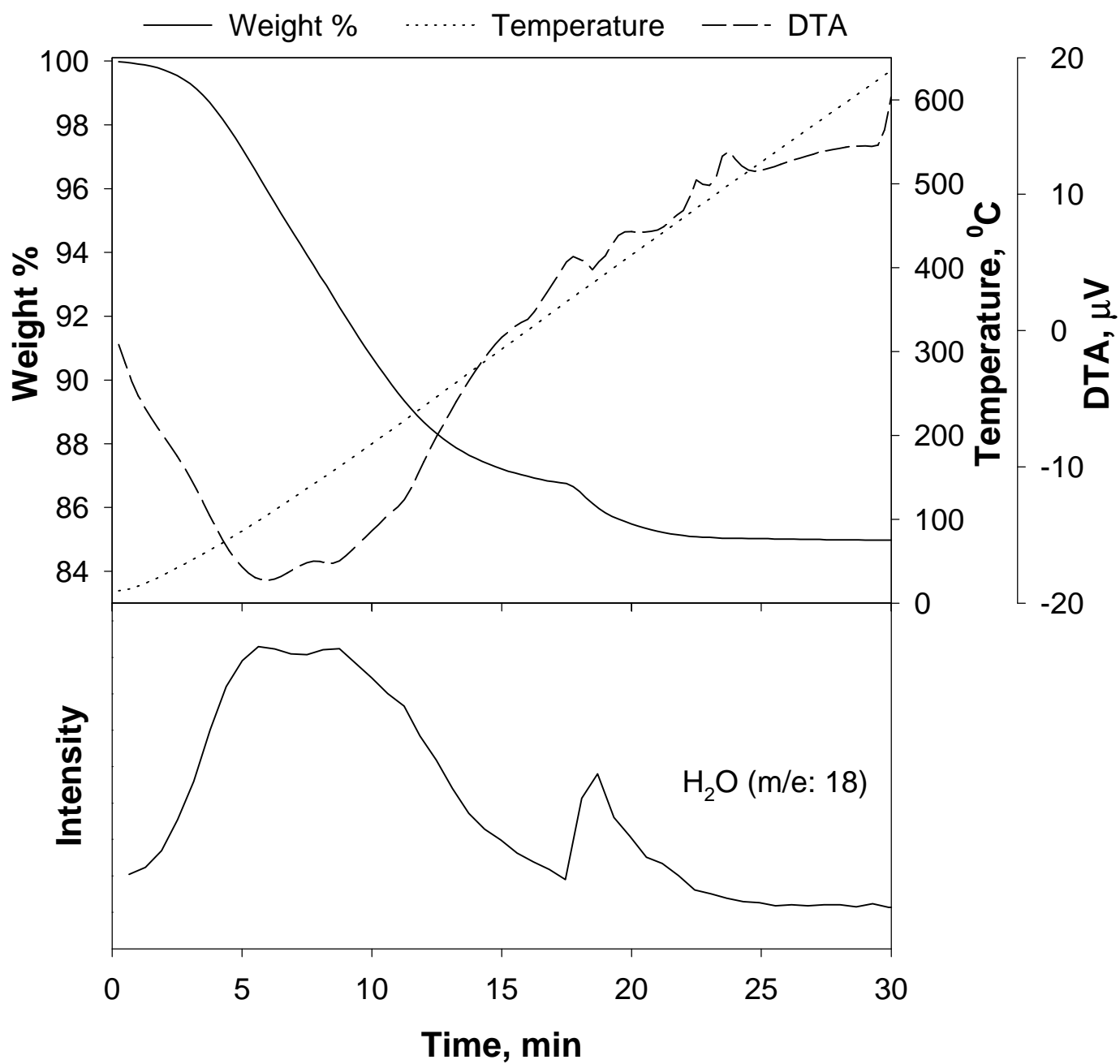


Figure 6. TG/MS spectra of NiPM in He.

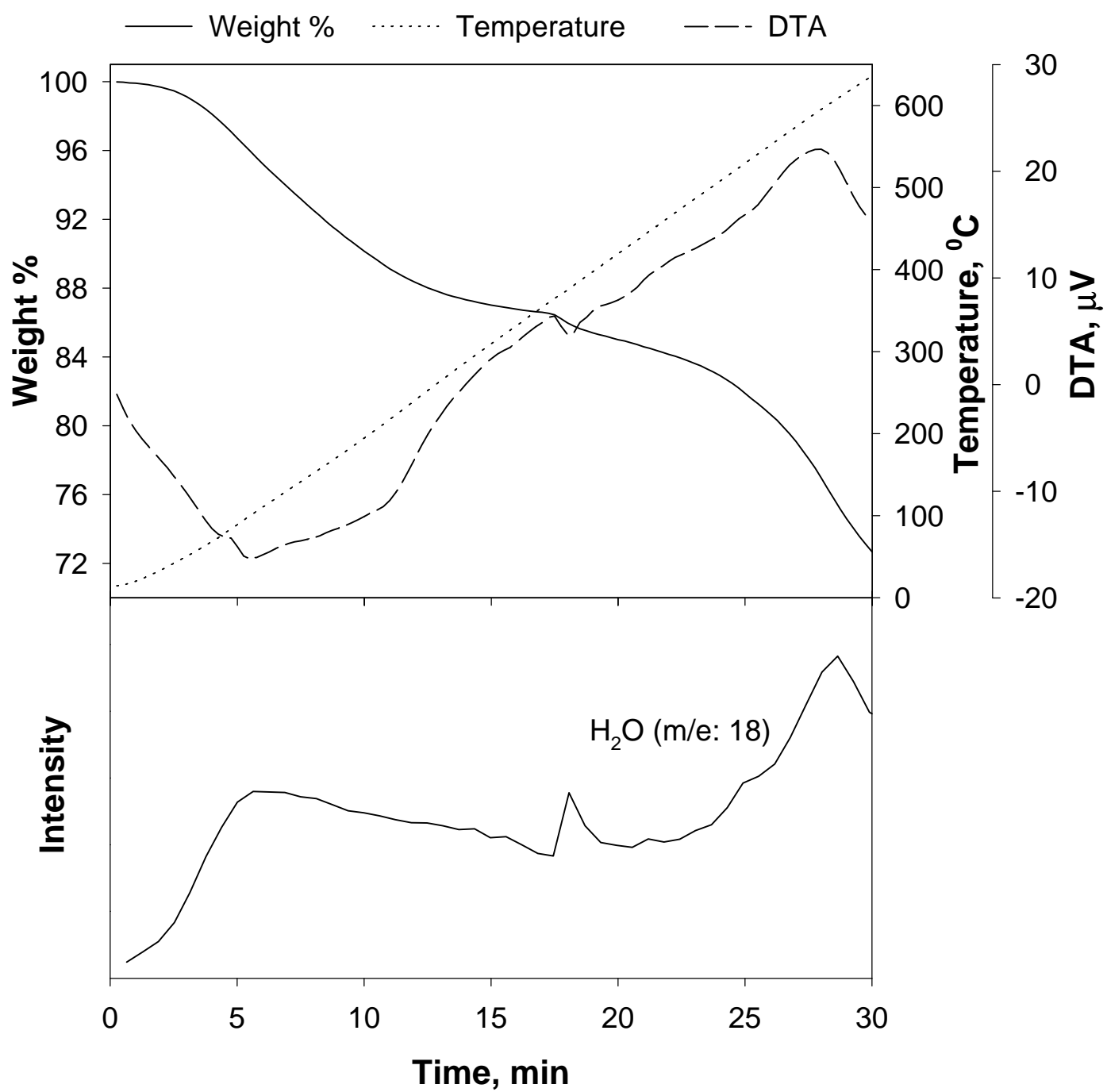


Figure 7. TG/MS spectra of NiPM in H<sub>2</sub>.

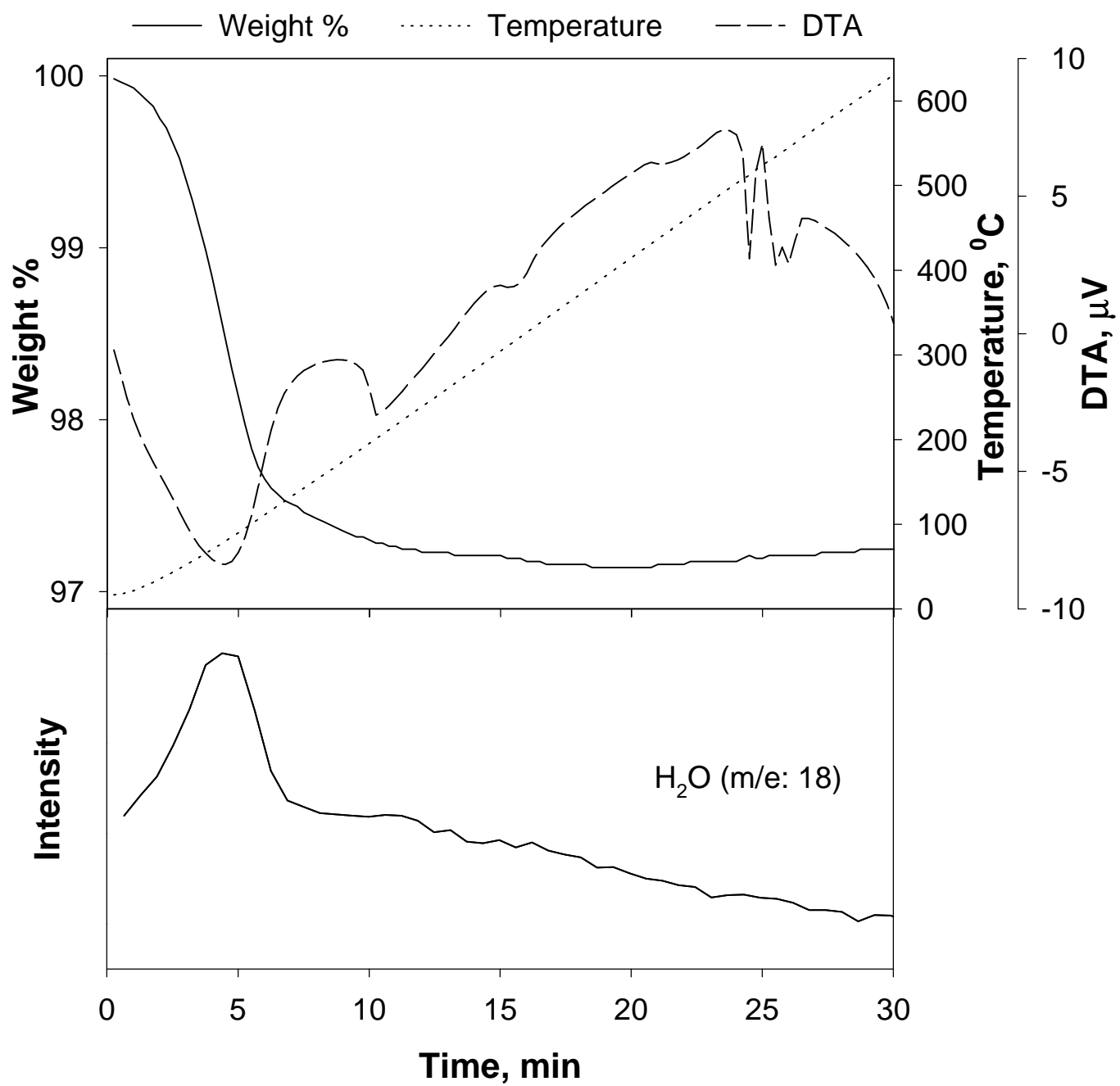


Figure 8. TG/MS spectra of KPM in He.

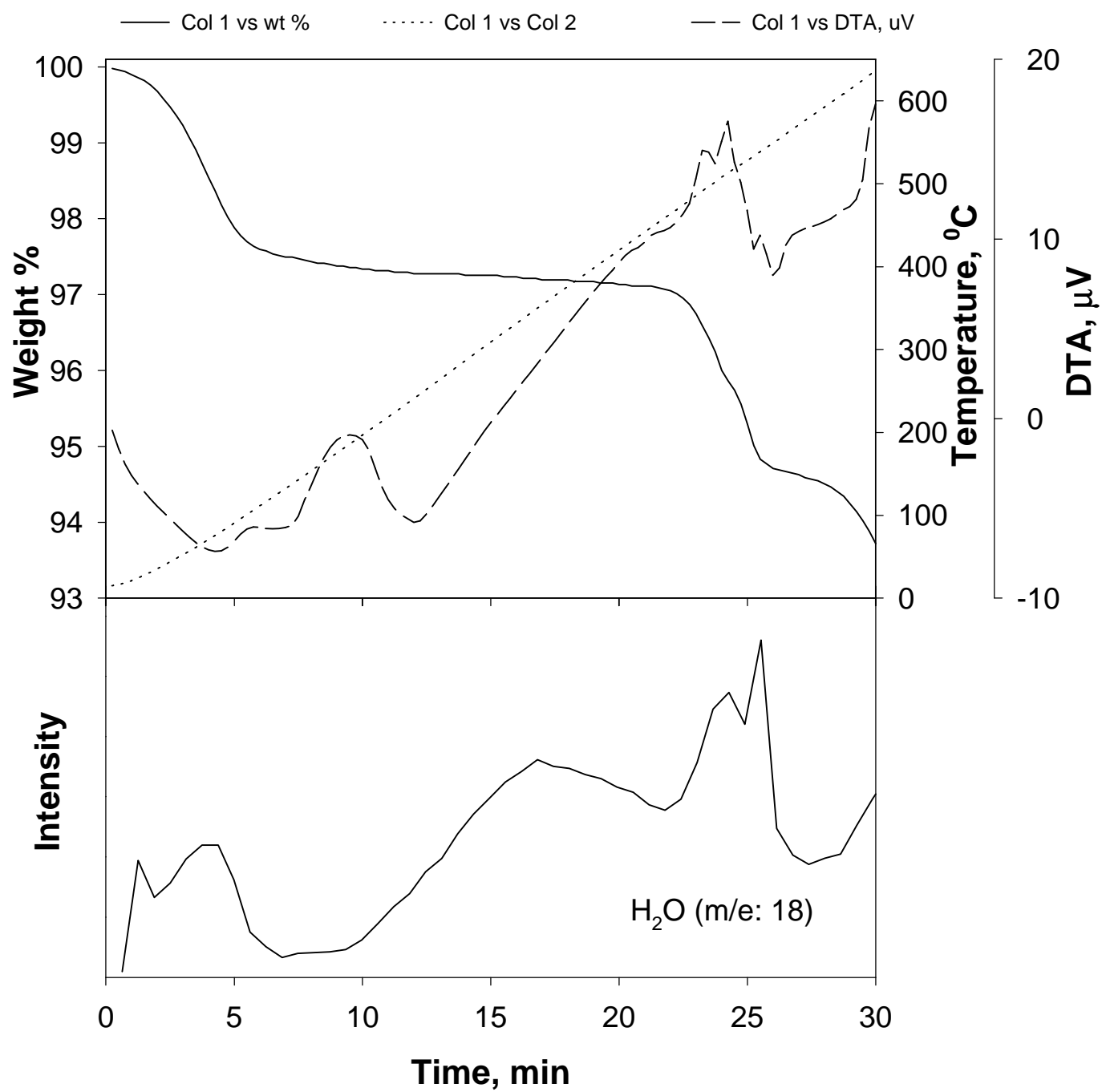


Figure 9. TG/MS spectra of KPM in H<sub>2</sub>.

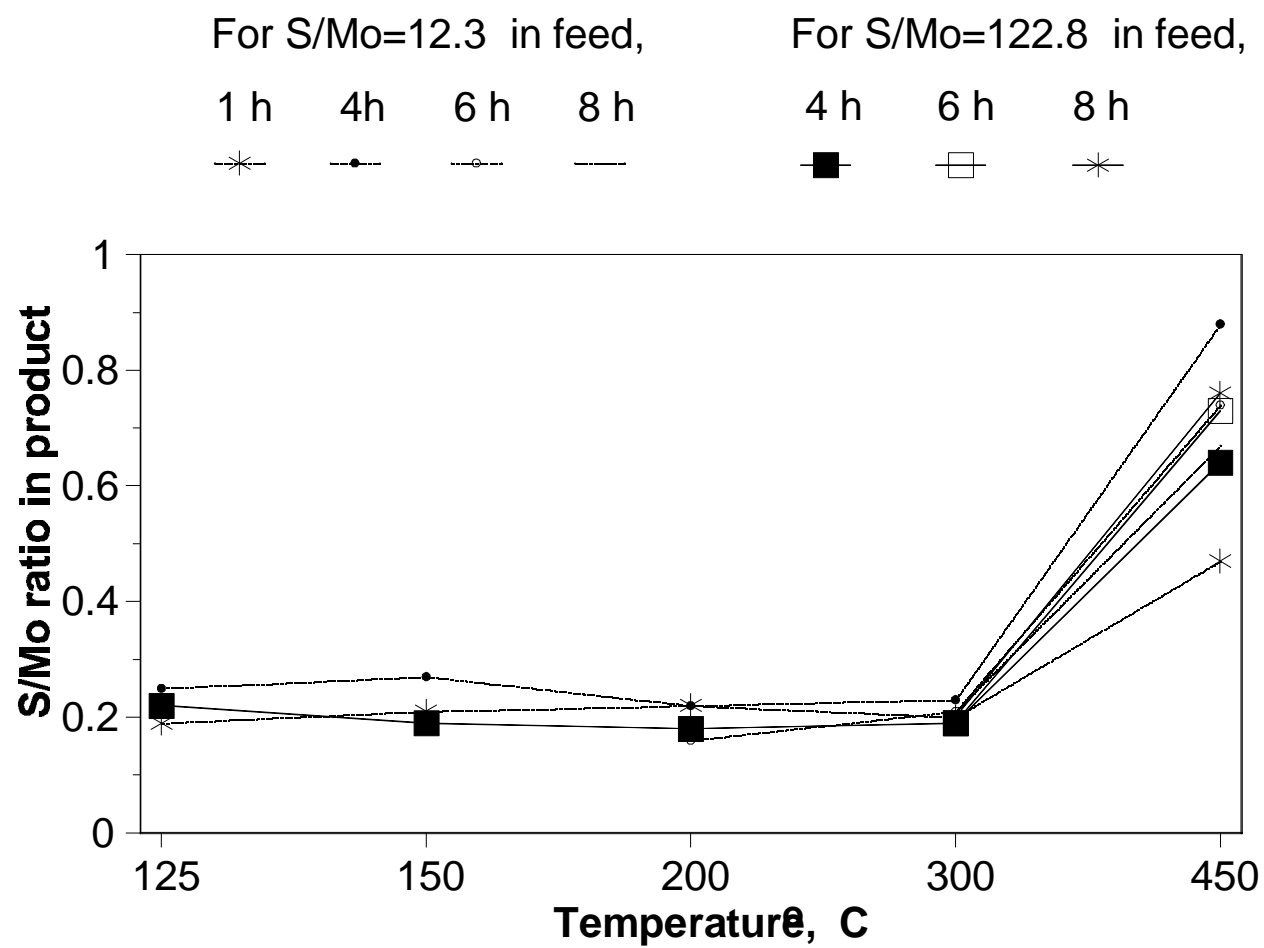


Figure 10. Sulfur uptake of PMA

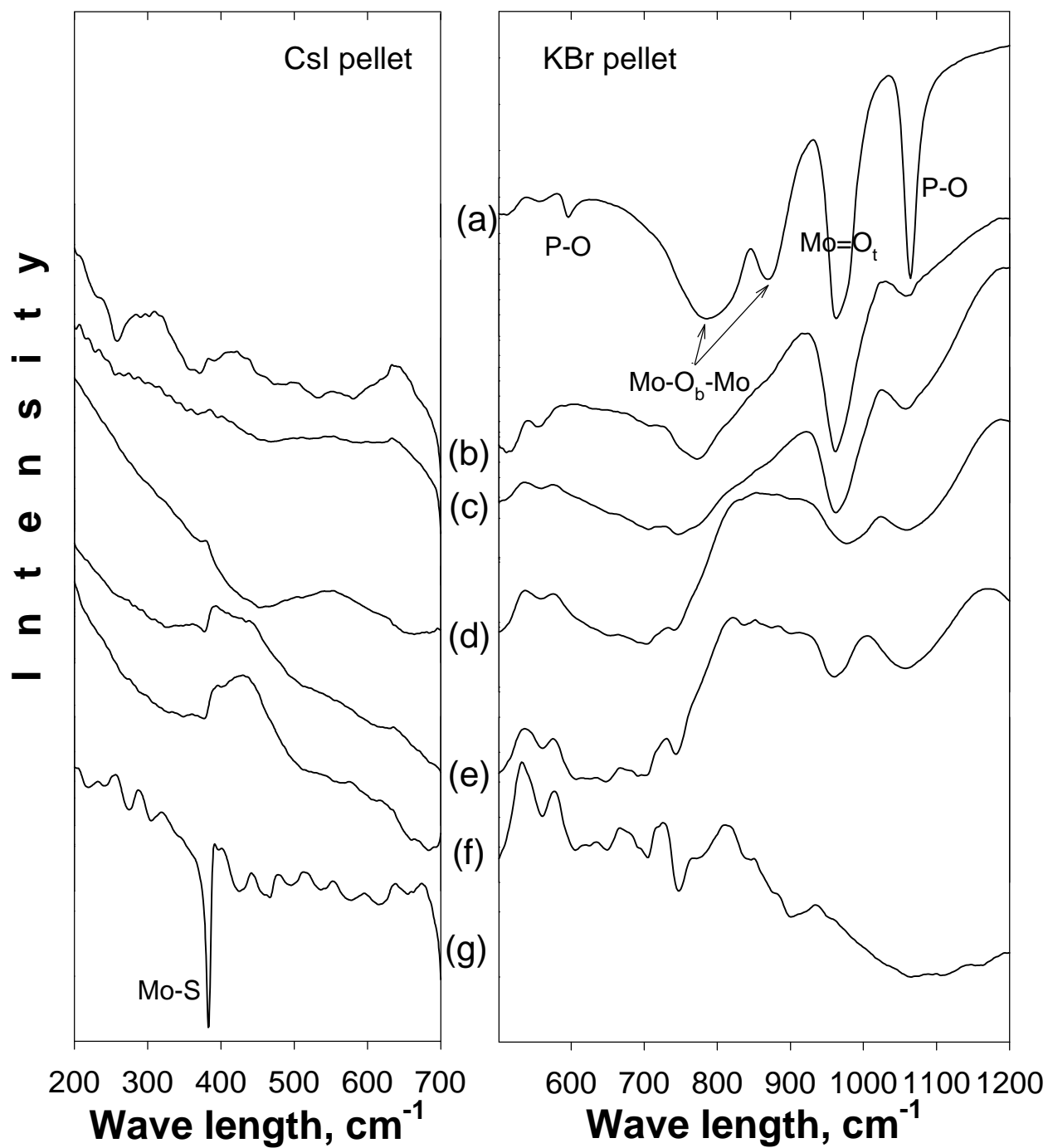


Figure 11. FT-IR spectra of (a) PMA, (b) PMA sulfided at 125<sup>0</sup>C, (c) PMA sulfided at 150<sup>0</sup>C, (d) PMA sulfided at 200<sup>0</sup>C, (e) PMA sulfided at 300<sup>0</sup>C, (f) PMA sulfided at 450<sup>0</sup>C and (g) MoS<sub>2</sub>.

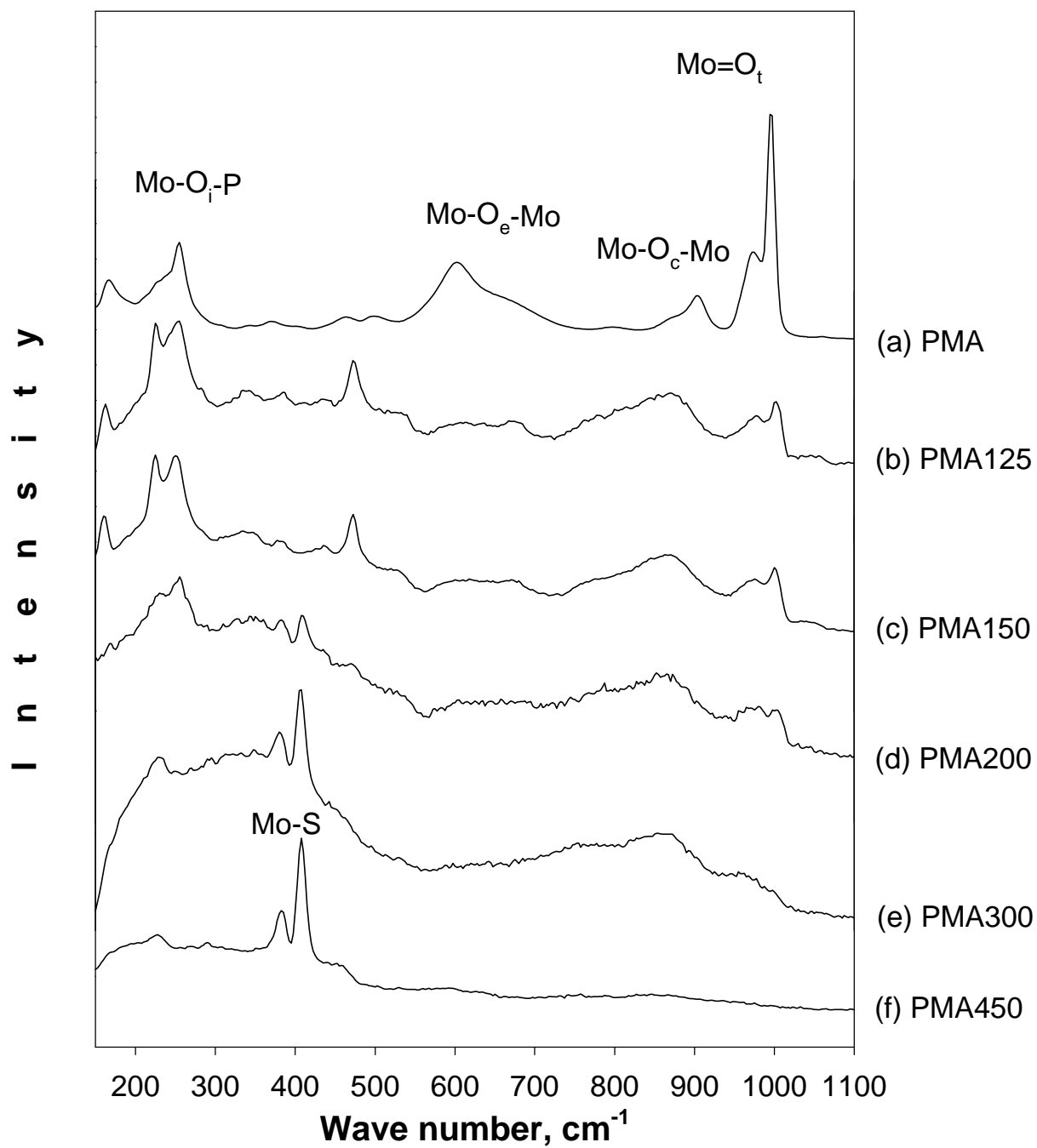


Figure 12. Raman spectra of (a) PMA, and PMA sulfided at (b) 125<sup>0</sup>C, (c) 150<sup>0</sup>C, (d) 200<sup>0</sup>C, (e) 300<sup>0</sup>C and (f) 450<sup>0</sup>C.

# HP Continuous Flow CSTR Modifications

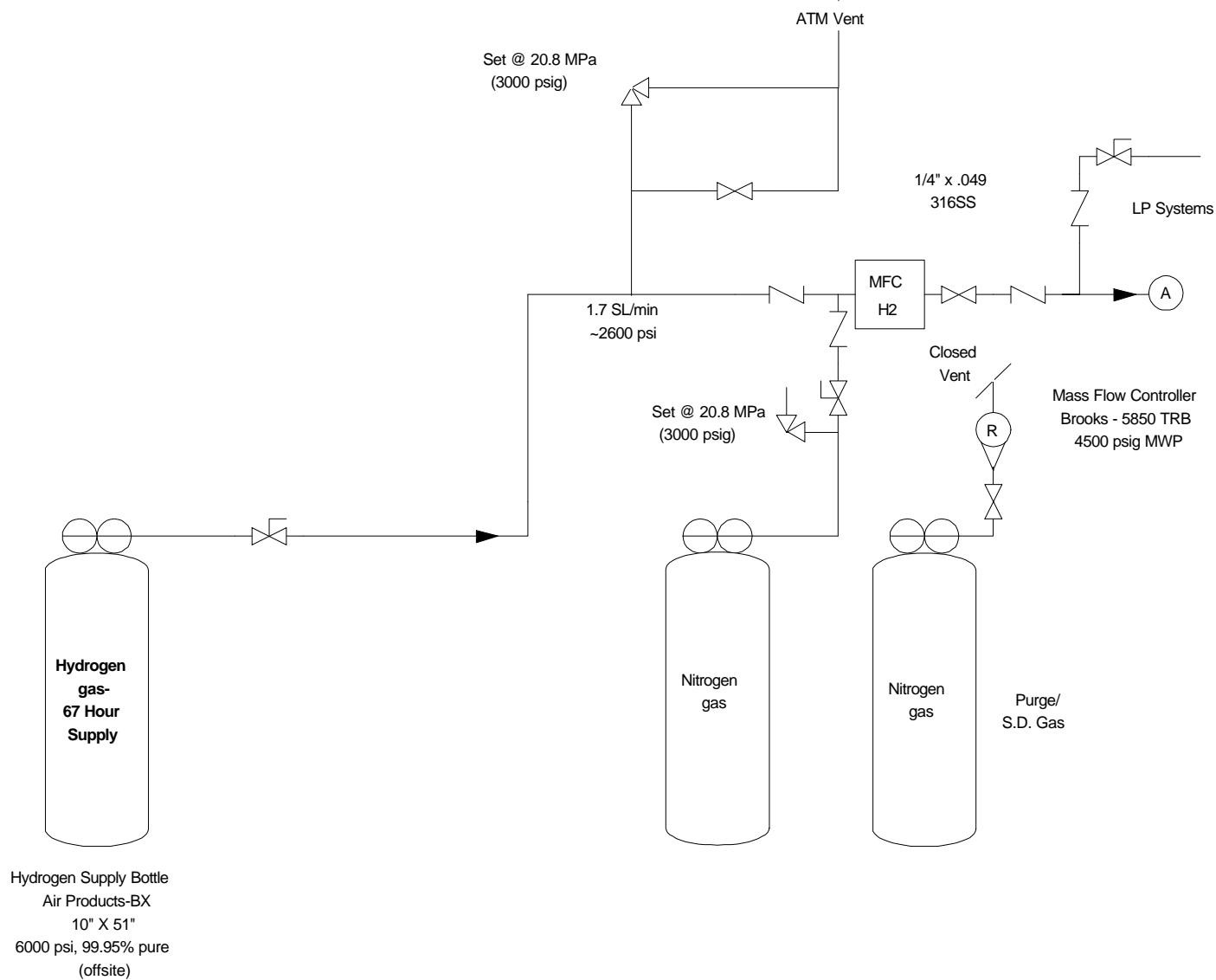


Figure 13. Gas supply system.

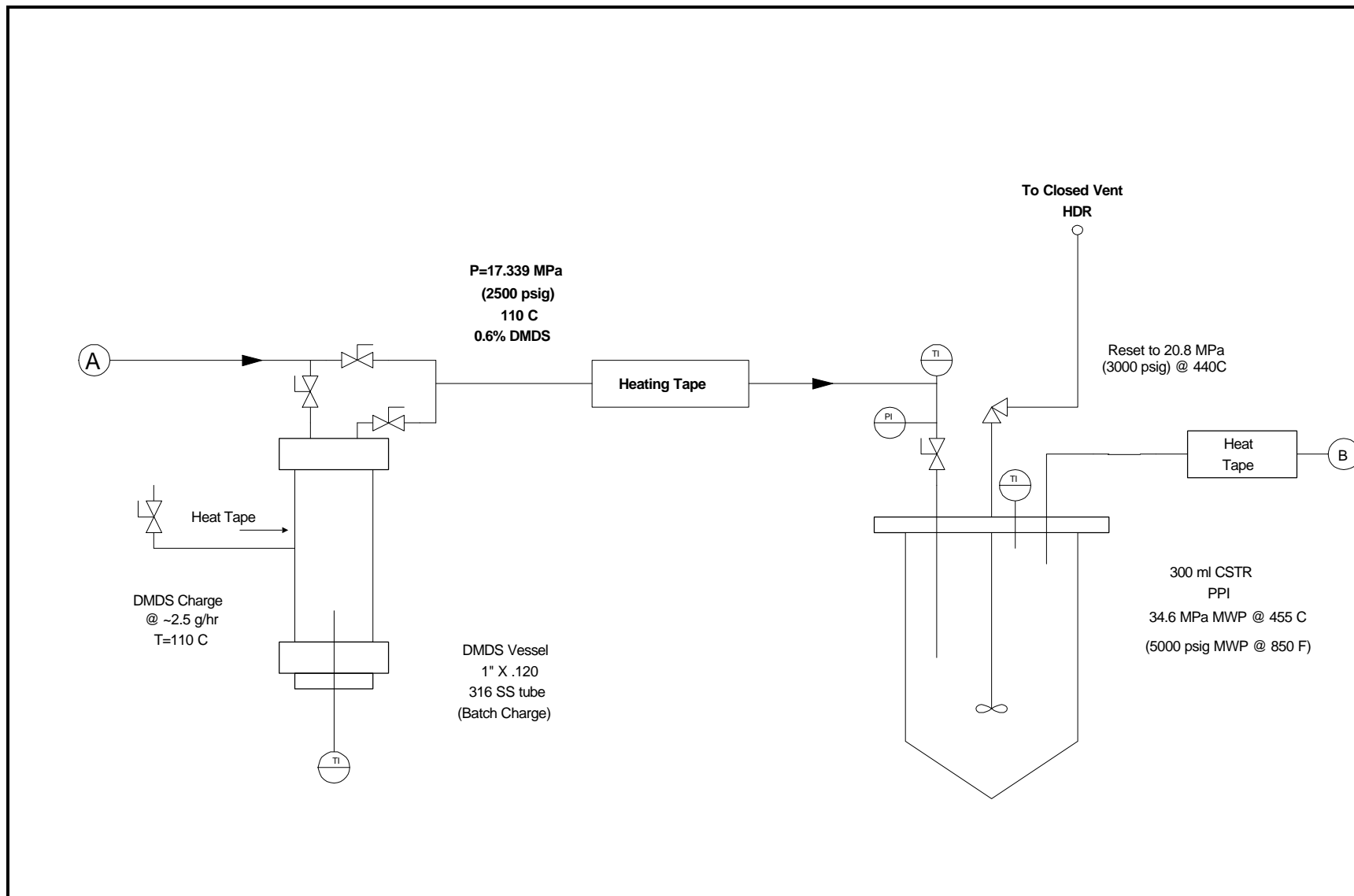


Figure 13 (cont.). DMS supply and reactor.

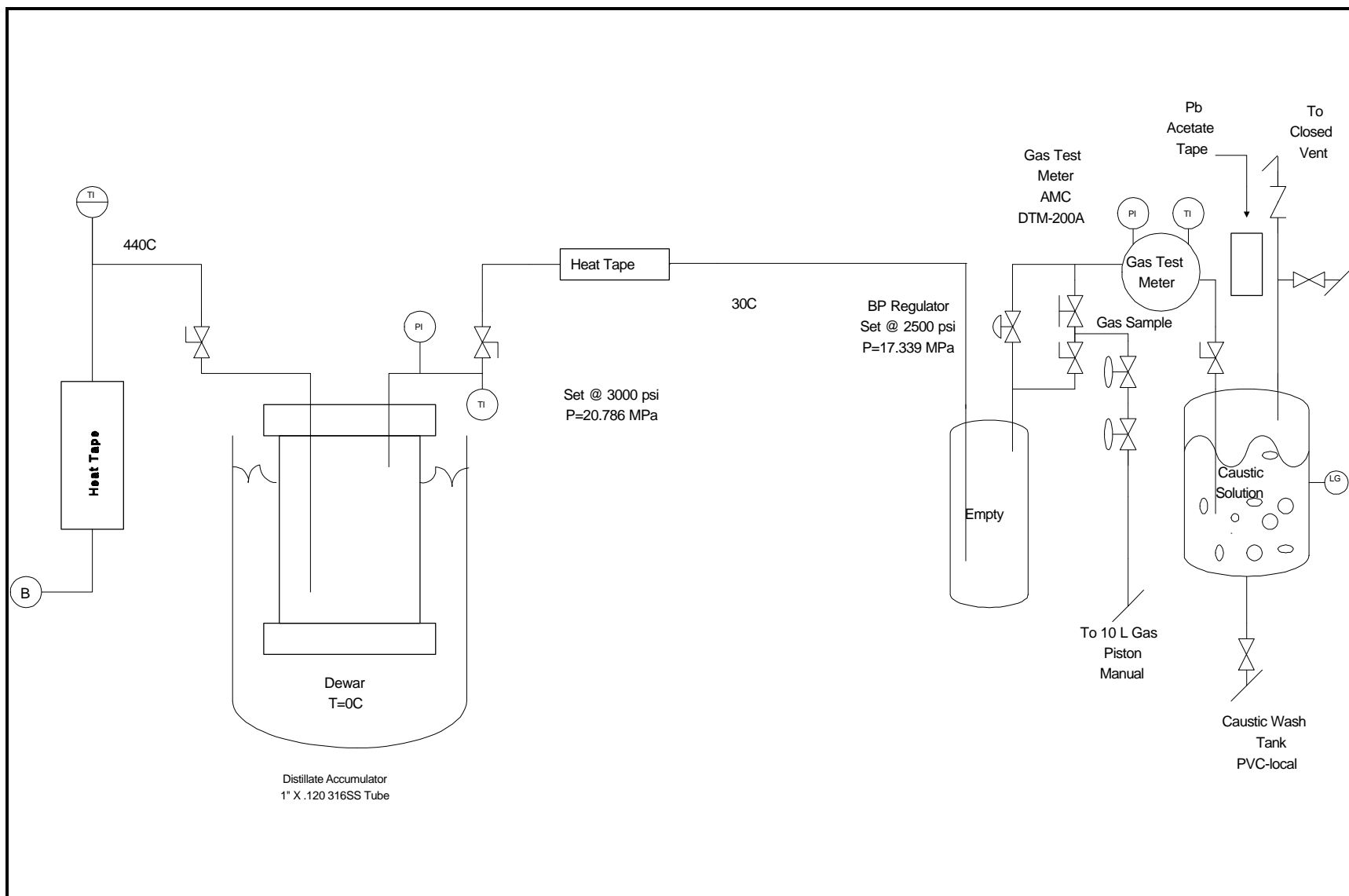


Figure 13 (cont.). Distillate collection and gas scrubbing

### High-Temp SIMDIS Analysis with Aromatic Correction

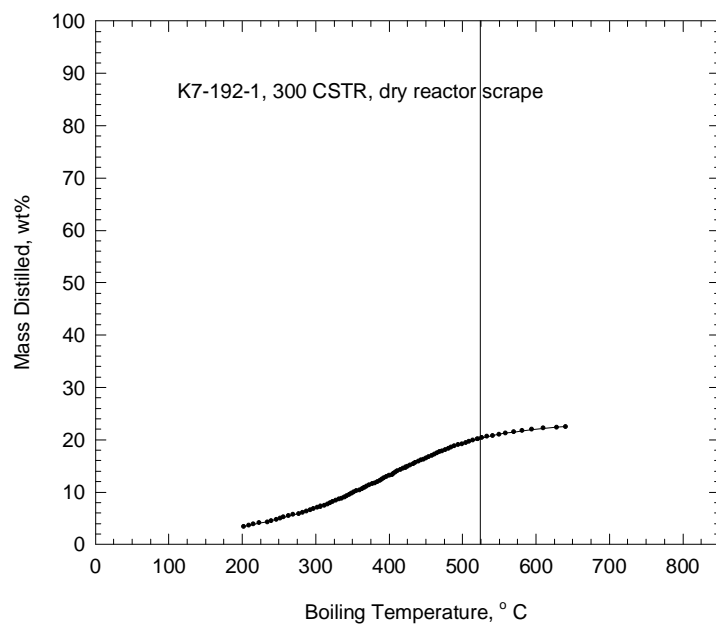


Figure 14. SIMDIS plot for "dry reactor scrape" sample.

## **SECTION TWO**

**CONSOL, Inc.**

**(Report for April-June 1997)**

September 22, 1997  
Report Period: April 1 - June 30, 1997

**SUBCONTRACT TITLE AND NUMBER:**

Subcontract UKRF-4-25582-92-76 to CONSOL Inc.  
Under DOE Contract No. DE-AC22-91PC91040, "Advanced Coal Liquefaction Concepts for the PETC Generic Bench-Scale Unit"

**SUBCONTRACTOR NAME:**

CONSOL Inc.  
Research & Development  
4000 Brownsville Road  
Library, PA 15129

**SUBCONTRACT PERIOD:** November 26, 1991 - October 31, 1997 (future extension to September 30, 1998, expected)

**PRINCIPAL INVESTIGATORS:** R. A. Winschel, G. A. Robbins

**SUBCONTRACT OBJECTIVES:** No change.

**SUMMARY OF TECHNICAL PROGRESS - OVERALL**

Determination of phenolics in Run ALC-1 product oils indicates that the phenol deoxygenation activity of the on-line hydrotreater (like the hydrogenation activity) remained high, even though the activity for nitrogen and sulfur removal was low. Characterization showed no evidence that the Mo and Ni in the vacuum bottoms from Run ALC-2 are organically associated. Recent batches of HTI's start-up oil (L-814) are so paraffinic that they would be unsuitable for use by Sandia as a feedstock for hydrotreating tests, as has been proposed.

CONSOL's near-term work plan is to provide assistance to Sandia regarding their hydrotreating tests and to complete the remaining action items from the Run ALC-3 planning meeting. The action items are to: 1) Perform slurry drying tests with agglomerates (tests with two oils at several temperatures each may be conducted). 2) Agglomerate the Ni/Mo-treated coal, and analyze the products to determine if the metals are retained with the coal. 3) Test concepts to reduce the cost of agglomeration (tests may be performed with emulsified oil, recycled water, and aeration).

A paper, "Oil Agglomeration at Low pH as a Pretreatment for Liquefaction of Wyoming (USA) Subbituminous Coal", covering the preparation and use of oil-agglomerated coal in Run ALC-1, was submitted for presentation at the 9th International Conference on Coal Science, September 7-12, 1997, Essen, Germany.

## **SUMMARY OF TECHNICAL PROGRESS - BY TASK**

### **Task 2 - Laboratory Support**

**Characterization of Samples From HTI Run ALC-1.** Phenolic -OH concentrations were determined on the hydrotreated and unhydrotreated separator overhead (SOH) oils from ALC-1. This work was conducted under DOE Contract DE-AC22-94PC93054. These analyses could not be completed during Run ALC-1, because the phenolic -OH method was not yet available on the new FTIR instrument. The hydrotreated oils were devoid of phenolic -OH, in spite of the high phenolic -OH concentration in the unhydrotreated first-stage SOH oils and poor catalyst activity for removal of nitrogen and sulfur. The catalyst lost activity when high-boiling material was inadvertently introduced into the product hydrotreater early in the run. Thus, the phenol deoxygenation activity, like the hydrogenation activity, remained high, even though the activity for nitrogen and sulfur removal was low.

**Characterization of Samples From HTI Run ALC-2.** The THF-solubles of the continuous vacuum still bottoms (CVSB) sample from the last condition of HTI Run ALC-2 were analyzed under DOE Contract DE-AC22-94PC93054 to determine if the Mo and Ni are present in oil-soluble form. The THF-solubles were prepared from the CVSB sample by pressure filtration with THF through a Whatman 42 paper (retains particles >2.5  $\mu\text{m}$ ), and evaporation of the THF from the filtrate. An analysis gave 72.3% THF solubles, 11.0% IOM, and 16.7% ash. The THF-soluble material contained 6 mg/kg Ni, 4 mg/kg Mo, a total of 416 mg/kg of the oxides of Si, Al, Fe, Ca, and Mg, and less than 0.1% ash (obtained using a separate aliquot of THF-soluble material). Thus, the occurrence of Ni and Mo is coincident with the occurrence of a trace amount of ash, and the Ni and Mo are not necessarily organically associated. The amount of Ni or Mo in the ash of the solubles (about 1% of the ash in the CVSB THF-solubles) is higher than in the ash of the coal or ashy process streams (about 600 mg/kg or less for Ni, 0.2% for Mo).

**Characterization of Sandia Hydrotreating Samples.** CONSOL reviewed Sandia's plan for hydrotreating work that will be conducted to help plan Run ALC-3. Discussions were held with

both Sandia and LDP Associates, and CONSOL's comments were provided by phone to F. Stohl of Sandia. Those discussions led to a question of whether the feed material to Sandia's most recent set of hydrotreating tests (the 524 °C<sup>-</sup> distillate of the pressure filter liquid (PFL) from HTI Run PB-01, period 16) was representative of coal-derived oil, rather than petroleum-derived oil. Hondo petroleum resid was the sole feedstock during periods 15 through 20 of Run PB-01 (Black Thunder Mine coal had been the sole feedstock for the earlier periods). Characterization data obtained recently on samples from HTI Run PB-01 under DOE Contract DE-AC22-94PC93054 indicate that Sandia's feedstock was predominantly coal-derived, even though it was produced when Hondo petroleum resid was the feed. CONSOL's 454 °C<sup>-</sup> distillate from the PFL from period 15 (the last day with 100% Black Thunder coal feed) contained 26% aromatic H. The corresponding PFL distillate from period 20 (the last day with 100% Hondo resid feed) contained only 10% aromatic H. Sandia's feed oil, the 524 °C<sup>-</sup> distillate from the PFL from period 16, contained 24% aromatic H.

LDP Associates proposed that the HTI start-up oil be used as the feedstock for Sandia's hydrotreating tests. To evaluate the suitability of HTI's start-up oil as a feed for hydrotreating tests, the proton distributions of samples of L-814 oil used for start-up and make-up in HTI Runs CMSL-9, ALC-1, and ALC-2 were compared. The Run ALC-2 L-814 oil is less aromatic and more paraffinic than the prior samples. If Run ALC-2 L-814 oil is representative of the current inventory, the current inventory may not be well-suited as a feedstock for Sandia hydrogenation tests. HTI provided CONSOL with a current sample of the oil for analysis.

### **Task 3 - Continuous Operations**

G. A. Robbins and R. A. Winschel participated in the preliminary planning meeting for Run ALC-3 on May 7 at CAER. CONSOL presented information regarding low-pH oil agglomeration and recycle solvent dewaxing/hydrotreatment. An overall plan for Run ALC-3 was developed. Ni/Mo catalyst will be fed by impregnation on the coal. All or most of the coal will be agglomerated at low pH, and the coal will be slurry-dried in the feed slurry tank. A 10-gal agglomerator will be used on-site, with preparation of one batch of agglomerates for every feed slurry preparation batch. No solvent dewaxing will be performed, but all of the second-stage distillate for product and recycle will be hydrotreated together, then cut into product and recycle oils. Only the material needed to reject solids (about 1/3 of the total flashed material) will be pressure-filtered, and the cake will be toluene washed. There will be two main conditions, consisting of about 10 days each, with perhaps two or more work-ups per condition. In one condition, catalyst-treated

coal will be agglomerated and fed. In the other condition, 90% of the coal will be untreated raw coal fed to agglomeration. The agglomerates will be fed to liquefaction with the remaining 10% of the uncleaned coal that was treated with enough catalyst for the entire lot (vector addition of catalyst). There may be an optional condition to liquefy raw coal.

#### **Task 4 - Technical Assessment**

CONSOL provided comments to CAER on their report summarizing the Run ALC-2 post-run meeting. HTI's revised report on Run ALC-2 was reviewed, and CONSOL's comments were provided to HTI. References on coal preparation were provided to LDP Associates to provide information that may be useful in evaluating the economics of oil agglomeration. A paper entitled "Oil Agglomeration at Low pH as a Pretreatment for Liquefaction of Wyoming (USA) Subbituminous Coal", authored by R. A. Winschel, G. A. Robbins, and J. Hu, was submitted to the International Conference on Coal Science, to be held September 1997 in Essen, Germany. The paper is appended.

R. A. Winschel  
Project Manager

/ls

## **APPENDIX**

### **OIL AGGLOMERATION AT LOW PH AS A PRETREATMENT FOR LIQUEFACTION OF WYOMING (USA) SUBBITUMINOUS COAL**

By R. A. Winschel, G. A. Robbins, and J. Hu

Submitted to the International Conference on Coal Science  
September 1997, Essen, Germany

# **Oil agglomeration at low pH as a pretreatment for liquefaction of Wyoming (USA) subbituminous coal**

R. A. Winschel<sup>a</sup>, G. A. Robbins<sup>a</sup>, and J. Hu<sup>b</sup>

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## **ABSTRACT**

Pulverized Wyoming subbituminous coal was beneficiated by low-pH oil agglomeration at CONSOL to prepare the coal for direct liquefaction. Conventional cleaning is not very effective in cleaning this coal; for example, conventional oil agglomeration only gives about 20% ash rejection. To improve ash rejection, the coal-water slurry was acidified to a pH of about 0.5. Oil agglomeration was effected with 33% (dry coal basis) of a coal-liquefaction recycle oil and high-shear mixing, producing agglomerates, which were separated from the rejected and dissolved inorganic matter by screening. The SO<sub>3</sub>-free-ash content of the coal was reduced by 40% (from 5.5% to 3.3%, dry basis) and the organic recovery was nearly 100%. The alkaline elements that are potential scaling agents and catalyst poisons were selectively rejected from the coal. Iron, a potential liquefaction catalyst, was selectively retained with the coal. A 600 kg batch of coal-oil agglomerates was produced. The liquefaction performance of this material was compared to that of the raw coal in the Hydrocarbon Technologies Inc. (HTI) 1.5 kg/h continuous-flow bench-unit. The agglomerates handled well and improved solids separation performance. The coal conversion with agglomerates (98% MAF) was higher than that with the raw coal (95% MAF), and the product yields (56% C<sub>4</sub>-343 °C distillate and 66% C<sub>4</sub>-524 °C distillate, MAF basis) were excellent.

**Keywords:** subbituminous coal, oil agglomeration, coal liquefaction

## **1. PRODUCTION OF OIL-AGGLOMERATED COAL**

Pulverized Wyoming subbituminous coal from the Black Thunder Mine (~10% H<sub>2</sub>O) was agglomerated with a vacuum distillate recycle oil from liquefaction of the same coal in the Wilsonville pilot plant (Run 263 end-of-run V-1074 vacuum distillate, b.pt. ~343-566 °C). Eight batches of agglomerates were produced as follows: 51 kg coal, 68 L of 70 °C water, and 1.45 L (2.5 kg) concentrated H<sub>2</sub>SO<sub>4</sub> were added to a 189 L baffled, open-topped, cylindrical agglomeration vessel equipped with a stirrer and a bottom drain.

The slurry was conditioned by stirring at 465 ppm for 60 min at 70 °C. Oil (15.4 kg) was added and the slurry was allowed to agglomerate for 90 min. The remaining two batches were made at slightly different conditions. The vessel contents were drained over a 50 mesh screen to separate the agglomerates from the aqueous screen underflow, and the agglomerates were rinsed with tap water until the wash water reached a pH of 4. The rinse water was combined with the screen underflow, sampled, and filtered to recover a cake and a filtrate. The agglomerates were spheroids with diameters of about 1 to 7 mm (typically 2 to 4 mm). The screen underflow was milky white from precipitated gypsum. The underflow contained virtually no organics, indicating near-quantitative recovery of organics. The agglomerates were dried to less than 10% moisture, either in a nitrogen-purged oven at 60 °C or spread out in a ventilated area for up to 5 days. Approximately 590 kg of dried agglomerates were prepared. The filter cake consisted mostly of 10 to 50  $\mu$ m gypsum crystals, about 89% purity, the remainder was primarily silica. The principal filtrate species include sulfates of Ca (major), Mg (medium), and Al, Fe, and Na (minor).

The analyses of the feeds and products (Table 1, Figure 1) indicate that Ca, Mg, and Na, potential catalyst poisons and source of scale deposits, are selectively rejected from the coal. About 80 wt % of the calcium in the coal was removed (Figures 1a and 1b). However, pyrite, a potential liquefaction catalyst, is selectively retained. Ash rejection was 42%  $\pm$  3% in the ten batches (ash content decreased to 3.3%  $\pm$  0.1% from 5.5%, MF ash-SO<sub>3</sub>-free and oil-free basis). Organic recovery was nearly quantitative.

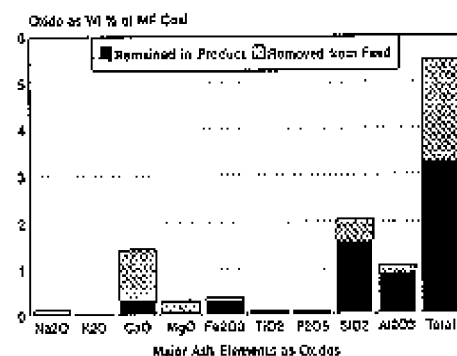


Figure 1a

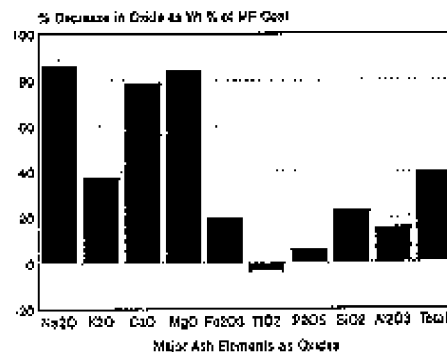


Figure 1b

## 2. LIQUEFACTION TESTING OF OIL-AGGLOMERATED COAL

The liquefaction objective was to demonstrate on HTI's bench unit the benefits of cleaning Black Thunder coal by oil agglomeration at low pH. The strategy was to operate with extinction recycle of 343 °C<sup>+</sup> material, adjusting space velocity as needed to produce a high quality 343 °C<sup>-</sup> hydrotreated product. Potential benefits to liquefaction

of this coal cleaning concept are to decrease the organic rejection, increase the coal conversion and yields, and decrease catalyst requirements. In the 25-day run, six days of baseline operation was performed with raw Black Thunder coal at Condition 1. Fourteen days of operation were conducted at alternate Conditions 2, 3, and 4 to evaluate the performance of the cleaned coal. The impact of agglomeration on catalyst make-up rate could not be determined because of uncertainties in the catalyst addition rate used.

The process conditions and results for Conditions 1, 3, and 4 are compared in Table 2. An increase in yields of heterogases and C<sub>1</sub>-C<sub>3</sub> gases was observed after Condition 1. Lowering the space velocity increased distillate yield and decreased resid yield. Coal conversion increased from about 95% to about 98%, and hydrogen consumption was lower. The cleaned coal showed improved solids separation performance. Liquefaction products boiling above about 343 °C were filtered to produce an oil for recycle and solids for rejection. When oil agglomerates were fed, filtration operations were faster and smoother. Toluene washing of the filter cake to recover additional oil for recycle also was more efficient (i.e., oil was extracted more completely). Rejected solids from liquefying the oil-agglomerated coal contained about half as much oil. These improvements may have resulted from the reduction in the quantity of solids processed when the agglomerates were fed, and, perhaps, selective rejection of organically-associated alkaline elements. Coal-oil agglomeration at low pH could have significant economic importance if it can be shown to increase the operability and on-stream factor for commercial liquefaction.

**Table 1.** Composition of agglomerating oil, feed coal, and agglomerated coal

	Agglom oil (as det'd )	Coal	Agglom 10-run avg (a)		Coal	Agglom 10-run avg
Moisture, wt % as det		9.91	7.54	<u>Major ash</u>		
Ash, wt % MF incl.		6.23	2.83	<u>elements,</u>		
SO <sub>3</sub>		11.78	9.65	<u>oxide wt % of</u>		
SO <sub>3</sub> , wt % of Ash	41759	28071	31734	<u>SO<sub>3</sub>-free ash</u>		
HHV, J/g (MF)				Na <sub>2</sub> O	1.75	0.41
				K <sub>2</sub> O	0.51	0.53
				CaO	25.78	8.99
<u>Ultimate, wt % MF,</u>				MgO	5.40	1.45
<u>SO<sub>3</sub>-free ash basis</u>	89.74	71.08	75.84	Fe <sub>2</sub> O <sub>3</sub>	6.66	8.87
carbon	8.81	4.69	6.13	TiO <sub>2</sub>	1.45	2.51
hydrogen	0.59	0.92	0.86	P <sub>2</sub> O <sub>5</sub>	1.36	2.13
nitrogen	0.03	0.50	0.73	SiO <sub>2</sub>	37.34	47.84
sulfur	0.84	17.32	13.88	Al <sub>2</sub> O <sub>3</sub>	19.14	26.93
oxygen (by diff)		5.50	2.56	Total	99.40	99.65
ash, SO <sub>3</sub> -free						

- (a) As a percent of the whole agglomerates, the agglomerates are composed of 7.5% ±1.2% moisture, 23.4% ±0.3% agglomerating oil, 2.4% ±0.1% SO<sub>3</sub>-free ash, and 66.7% ±1.0% MAF coal.

**Table 2.** Liquefaction conditions and process performance results from Run ALC-1

Condition Coal type	1 raw	3 agglom	4 agglom
<u>Net normalized yields, wt % MAF coal</u>			
C <sub>1</sub> -C <sub>3</sub> in gases	9.42	10.84	12.40
C <sub>4</sub> -343 °C	53.23	50.96	56.59
343-524 °C	15.81	10.35	9.49
524 °C <sup>+</sup>	4.33	10.38	4.56
Unconverted coal	5.04	2.42	2.51
Water yield by material balance	13.83	16.19	16.20
CO <sub>x</sub>	5.92	4.44	4.27
NH <sub>3</sub>	0.73	0.62	0.90
H <sub>2</sub> S	-0.77	0.03	-0.09
Hydrogen consumption	7.5	6.2	6.8
<u>Process conditions</u>			
Space velocity (each reactor) kg MF coal/h/m <sup>3</sup>	675	550	418
Target fresh catalyst conc., metal mg/kg MF coal			
Mo	100	71	68
Fe	10000	7120	6810

Other conditions: 1.60 recycle to MF coal ratio; 0.20 recycle solids to MF coal ratio; 15MPa system pressure, reactor temperatures were ~442 °C (first stage) and 452 °C (second stage)

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## Abbreviations and Acronyms

AF	Ash free
AHM	Ammonium heptamolybdate
ALC	Advance liquefaction concepts
AN	Anhydrite
AOTM	Ammonium dioxodithiomolybdate
API	American Petroleum Institute
APTM	Ammonium polythiomolybdate
ASOH	Atmospheric still overhead
ASTM	American Society for Testing Materials
ATTM	Ammonium tetrathiomolybdate
BT	Black Thunder Mine
CC	Calcium carbonate
CAER	Center for Applied Energy Research
CAS	Continuous atmospheric still
CMSL	Run designation used by HTI
CoPM	Cobalt phosphomolybdate
CST	Catalyst screening test
CVS	Continuous vacuum still
CVSOH	Continuous vacuum still overhead
CVSB	Continuous vacuum still bottoms
DAF	Dried and ash free
DW-HT	Dewaxed-hydrotreated
DW-HT-VSOH	Dewaxed hydrotreated vacuum still overhead
DW-VSOH	Dewaxed-vacuum still overhead
DMDS	Dimethyl disulfide
EDS	Energy Dispersive Spectroscopy
EO	Extracted oil
EOVSB	Extracted oil vacuum still bottoms
ES	Extracted filter cake
FBP	Final boiling point
FTIR	Fourier transform infrared
FS	Ferrous sulfate
GC	Gas Chromatograph
HC	Hydrocarbon
HTI	Hydrocarbon Technologies, Inc.
HTU	Hydrotreater unit
IBP	Initial boiling point
IOM	Insoluble organic matter
J-1	Charge pump
J-2	Charge pump
K-1	First stage reactor
K-2	2nd-stage reactor
K-3	In-line hydrotreater

KA	Kaolinite
KPM	Potassium phosphomolybdate
L-814	End-of-run makeup oil in Tank #4 from HTI's POC-02 run
MAF	Moisture and ash free
NiPM	Nickel phosphomolybdate
O-1	2nd-stage hot separator
O1-A	1st stage hot separator
O-2	2nd stage cold separator
O-2A	1st stage cold separator
O-3	2nd stage hot separator bottom flasher
OA	Oil agglomerated
P-2	Feed tank
PFC	Pressure filter cake
PFL	Pressure filter liquid
PMA	Phosphomolybdic acid
PY	Pyrrhotite
POC	Proof of concept
PPT	Precipitate
QI	Quinoline insolubles
QZ	Quartz
RPS	Reduced pressure still
RPSB	Reduced pressure still bottoms
RPSOH	Reduced pressure still overhead
SEM	Scanning electron microscopy
SIMDIS	Simulated distillation
sL	Standard liters
sLpm	Standard liters per minute
SOH	Separator overhead
SSSY	Speculative steady-state yields
TBP	True boiling point
TE	Toluene extraction unit
TEO	Toluene extracted oil
TES	Toluene extracted solid
TGA	Thermogravimetric analysis
TG/MS	Thermogravimetric-mass spectrometric analysis
THF	Tetrahydrofuran
TNPS	Ditertiarynonyl polysulfide
UK	University of Kentucky
VT	Vaterite
VSb	Vacuum still bottoms
VSOH	Vacuum still overhead
XRD	Xray diffraction